

Photo-Rechargeable Zinc-Ion Capacitors using V₂O₅ – Activated Carbon Electrodes

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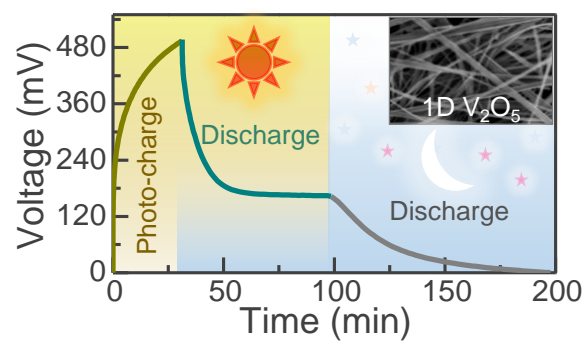
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Abstract

Electrochemical energy storage devices that can harvest energy from the environment and store it are increasingly important to address both energy poverty in developing parts of the world, as well as powering off-grid autonomous devices. Currently, batteries or supercapacitors connected to solar cells are used for these applications, but these frequently suffer from voltage mismatches and inefficiencies in the device packaging. This paper presents an optically and electrochemically active electrode for photo-rechargeable zinc-ion capacitors using vanadium oxide nanofibers. These rely on photo-excited charge carrier separation to charge the capacitors without any external photovoltaic or electrical devices. We found that silver nanowires are better than carbon based conductive additives as they support photo-excited holes transport and provides light scattering centers that enhance visible light absorption. The proposed capacitors show a ~ 63% capacity increase under illumination, photo-recharge in 30 minutes and ~ 99% capacity retention over 4000 cycles.

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To date, many communities in developing countries still lack access to environmentally benign and cost-effective energy solutions. This energy poverty is a grand challenge for off-grid communities for which few viable energy sources are available. The most common solution is to combine photovoltaic devices with batteries or electrochemical capacitors.¹⁻⁵ A number of academic papers have looked into integrating these devices efficiently. For instance, Hui *et al.* proposed a portable and efficient solar-rechargeable battery system based on a perovskite solar module integrated with an aluminum ion battery;⁶ Xu *et al.* reported a lithium-ion battery (LIB) integrated with perovskite solar cells;⁷ Liu and co-workers considered polypyrrole-based supercapacitors recharged by silicon nanowire/polymer hybrid solar cell.⁸ However, integrated energy harvesting and storing devices introduce some challenges in device packaging efficiency and ohmic transport losses.^{9,10} Further, the output voltage of photovoltaic cells is often insufficient to fully charge the batteries or capacitors, which then requires additional electronics that add to the cost of the devices.^{7,10-12}

Recently, there have been some developments towards electrodes of batteries and capacitors that can directly harvest solar power without the need for solar cells, thereby offering an elegant solution for the challenges listed above.^{10,13-19} Here we present a new light rechargeable electrochemical capacitors. In general, electrochemical supercapacitors have drawn attention in the scientific community because of their high power density, fast charge, long cycling life and safe operation.²⁰ However, they suffer from low energy density, and to bridge the gap in power density and energy density between supercapacitors and LIBs, a new class of energy storage devices known as metal ion capacitors have been proposed.^{21,22} Recently, aqueous zinc-ion capacitors (ZICs) have been studied because of their environmental friendliness and low cost compared to non-aqueous lithium or sodium ion capacitors.^{23,24}

Recently, a photo-rechargeable ZIC (hv-ZIC) was proposed using graphitic carbon nitride as the active material.²⁵ This system achieved a light conversion efficiencies of $\sim 0.01\%$, photo-charge energy densities of 0.7 Wh kg^{-1} and photo-charge capacities of 11.4 F g^{-1} .²⁵ Here, we report an improved hv-ZIC system using vanadium pentoxide (V_2O_5) based photoanodes with activated carbon (AC) cathodes as illustrated in **Figure 1a** (the photo-charging mechanism is discussed further on). V_2O_5 is selected here because of its bandgap in the visible light spectrum and its ability to reversibly intercalate/deintercalate Zn ions (see further). The energy band alignment of the photoanodes is studied using chirality sorted (6,5) semi-conducting single walled carbon nanotubes (SCNTs), conducting multi walled carbon nanotubes (MCNTs) and silver (Ag) nanowires. These electrodes allow for light charging without external circuit, with the best photo conversion efficiency achieved for the $\text{Ag@V}_2\text{O}_5$ system ($\sim 0.05\%$). The photo-charge energy density is improved from $\sim 0.7 \text{ Wh kg}^{-1}$ to $\sim 4.8 \text{ Wh kg}^{-1}$ and the capacity from $\sim 11.4 \text{ F g}^{-1}$ to $\sim 138 \text{ F g}^{-1}$ compared to previous hv-ZICs²⁵ (these are improvements of 7 and 12 fold respectively). Finally, energy densities of $\sim 53 \text{ Wh kg}^{-1}$ are achieved, which is comparable to state of the art asymmetric supercapacitors, and the devices achieved stable cycling (4000 cycles) both in dark and light conditions.

One dimensional V_2O_5 nanofibers are explored to improve the charge generation throughout the material and to allow efficient photo-charge conduction along the nanofiber length.²⁶ These nanofibres are synthesized via a hydrothermal process (see experimental section). **Figure 1b, c** show an SEM image and EDS mapping of the V_2O_5 fibers, which have typical diameters of 20 – 150 nm (a representative EDS spectrum is provided in **Figure 1d**). The high-resolution TEM inset in **Figure 1b** shows an interplanar spacing of $\sim 0.34 \text{ nm}$ that corresponds to (110) planes of orthorhombic V_2O_5 crystals which is confirmed by XRD in **Figure 1e** (space group: Pmmn (59); JCPDS card no: 03-065-0131). Moreover, Raman spectrum (**Figure S1**) shows characteristic peaks of V_2O_5 which are discussed in supporting information. UV-Vis analysis

in **Figure 1f** shows the V_2O_5 nanofibers have a band edge of ~ 564 nm (~ 2.2 eV, the inset shows the first derivative of absorbance with respect to energy vs energy plot).^{26,27}

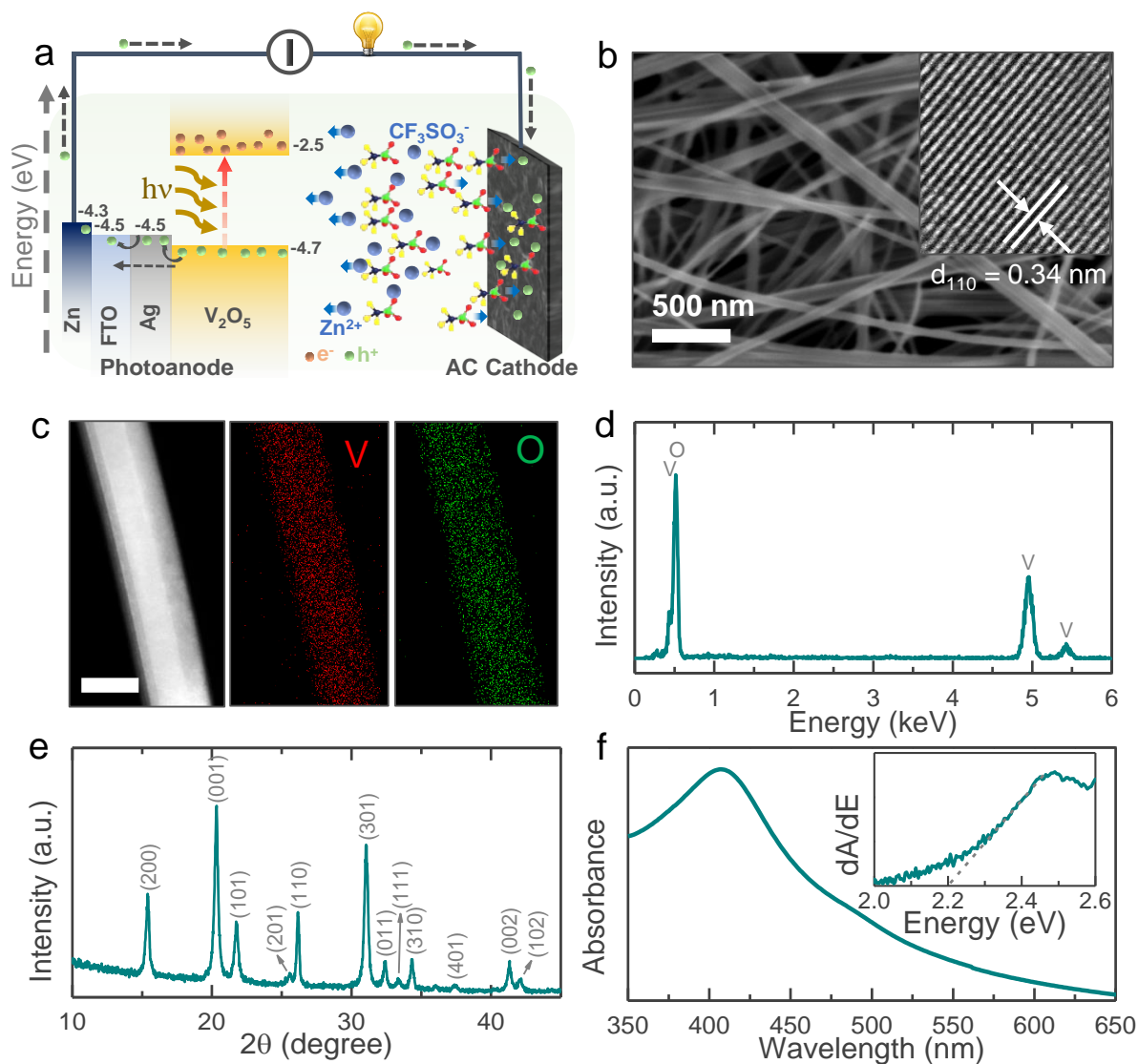


Figure 1. (a) Schematic representation of $h\nu$ -ZICs using $Ag@V_2O_5$ photoanodes and AC cathodes. (b) SEM and TEM (inset) image of V_2O_5 nanofibers. (c,d) Elemental mappings and EDS spectrum of a single nanofiber. Scale bar: 50 nm. (e) XRD pattern of V_2O_5 nanofibers (space group: $Pmmn$ (59); JCPDS card no: 03-065-0131). (f) Absorption spectrum (inset shows the first derivative of absorbance with respect to energy vs energy plot).

The photoanodes are fabricated by mixing same wt% loading of SCNTs, MCNTs or Ag nanowires (see experimental section, **Figure S2a-c** show SEM images) with V₂O₅ nanofibers (these will be referred to as SCNTs@V₂O₅, MCNTs@V₂O₅ and Ag@V₂O₅, respectively). First, to understand the dynamics of the photo-charge carriers, we measure electrical photo-responses of the pristine V₂O₅, SCNTs@V₂O₅, MCNTs@V₂O₅ and Ag@V₂O₅ materials by coating the material on photodetectors using gold (Au) interdigitated electrodes (IDEs, see experimental section). The same amount of photoanode material is drop casted on each Au IDEs followed by current-voltage (IV) measurements shown in **Figure 2a** for Ag@V₂O₅ (IV responses of V₂O₅, SCNTs@V₂O₅ and MCNTs@V₂O₅ are shown in **Figure S3**). The current responses of the photodetectors increase when exposed to light ($\lambda \sim 455$ nm) due to the V₂O₅ nanofibers. The current enhancements ($\frac{I_{ph}-I_d}{I_d} \times 100\%$; where I_d and I_{ph} are current densities in dark and illuminated conditions) of the photodetectors at different bias voltages are shown in **Figure 2b**. The high current enhancement of Ag@V₂O₅ photodetectors ($\sim 31.9\%$ at 1V) is probably due to the presence of multiple light scattering centers from the Ag nanowires, which increases light interaction probabilities with V₂O₅ (see further).²⁸⁻³⁰ However, lower current enhancements of $\sim 12.3\%$ and $\sim 1.4\%$ at 1 V of the SCNTs@V₂O₅ and MCNTs@V₂O₅ photodetectors as compared to pristine V₂O₅ photodetector ($\sim 18.9\%$ at 1 V) could be due to the absorption of light by SCNTs and MCNTs (these do not contribute to photo-current, see further). Likewise, cyclic current enhancements of the photodetectors under periodic illuminated and dark states at bias voltage of 1 V shown in **Figure 2c** shows better current enhancement of Ag@V₂O₅ photodetector as compared to other photodetectors. The slow dark current decays after switched off illumination of the photodetectors could be caused by oxygen vacancies related defects states.^{31,32} The electrical measurements suggest that introduction of Ag with V₂O₅ enhance the overall photo-sensitivity as compared to the pristine counterpart. The absorbance (**Figure S4a**) and transmission spectra (**Figure 2d**) confirmed absorption of

light by SCNTs, MCNTs and Ag nanowires. Further, steady state photoluminescence (PL) (**Figure S4b**) and time resolved photoluminescence (TRPL) measurements (**Figure 2e**) are used to understand the photo-charge carrier dynamics of the photoanodes. **Figure 2e** shows the TRPL of the samples fitted using a bi-exponential time decay model.³³ Interestingly, the average charge carrier lifetime of the Ag@V₂O₅ significantly increased (~ 40%) as compared to that of pristine V₂O₅ counterpart. However, the carrier lifetimes of the SCNTs@V₂O₅ and MCNTs@V₂O₅ samples are decreased (~ 24% and ~ 23%) compared to that of V₂O₅. The observed enhancement in the steady state PL intensity and TRPL lifetime of Ag@V₂O₅ could be due to a combination of light scattering and potential defect passivation. Similar, bi-exponential or tri-exponential PL time decays associated with V₂O₅ systems have been observed earlier.^{34,35}

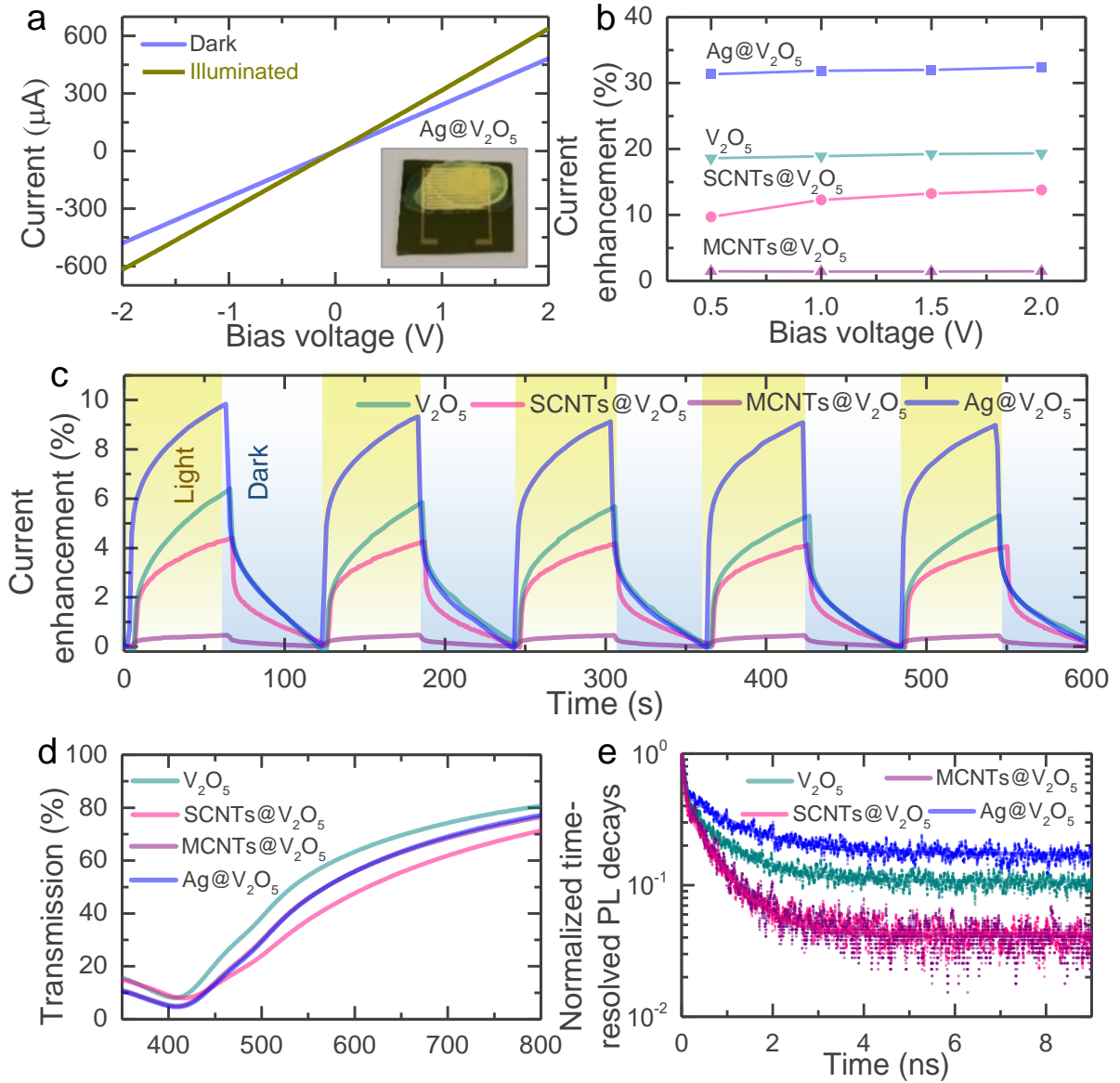


Figure 2. (a) IV profiles of the Ag@V₂O₅ photodetector in dark and illuminated conditions ($\lambda \sim 455$ nm). (b) Current enhancements of the pristine V₂O₅, SCNTs@V₂O₅, MCNTs@V₂O₅ and Ag@V₂O₅ photodetectors at different bias voltages of 0.5 V, 1.0 V, 1.5 V and 2.0 V. (c) Cyclic current enhancements of the photodetectors under periodic illuminated and dark conditions at bias voltage of 1 V. (d) Transmission spectra of pristine V₂O₅, SCNTs@V₂O₅, MCNTs@V₂O₅ and Ag@V₂O₅ samples. (e) Time resolved PL decays of the V₂O₅, SCNTs@V₂O₅,

MCNTs@V₂O₅ and Ag@V₂O₅ samples (407 nm pulsed excitation, repetition rate of 40MHz and fluence of 10 nJ cm⁻² pulse⁻¹).

Next, photo-capacitors are prepared by drop casting a mixture of V₂O₅ and Ag nanowires, SWCNTs or MWCNTs on fluorine doped tin oxide (FTO) coated transparent glass substrates (see SEM images in **Figure S5a-d** and cross section SEM in **Figure S6**). These substrates are mounted in CR2450 coin cell, in which ~ 8 mm diameter hole are machined to allow for illumination of the anodes as depicted in **Figure S7a,b**. Zn strips were used to contact the FTO to the coin cell to allow efficient photo excited holes transportation (see **Figure S7b** and **Figure 1a**). Some Zn stripping and plating might take place on this strip, but based on the electrochemical analysis, the contribution of this process to the overall capacity is negligible. Then, the mass ratio of cathode (activated carbon (AC), **Figure S7c** shows SEM image) to photoanode was optimized to obtain the optimum cell capacity, which is found to be 1.3:1 as shown in **Figure S8**. Finally, we used glass microfiber separators and ~ 150 µL of 3 M Zn(CF₃SO₃)₂ aqueous electrolyte.

Cyclic voltammetry (CV) of the pristine V₂O₅, SCNTs@V₂O₅, MCNTs@V₂O₅ and Ag@V₂O₅ hv-ZICs was carried out in in dark and light conditions ($\lambda \sim 455$ nm, intensity ~ 12 mW cm⁻²) to investigate the influence of light on the device current (see **Figure S9**). The CVs of the Ag@V₂O₅ hv-ZIC at scan rates of 50 mV s⁻¹, 500 mV s⁻¹ and 1000 mV s⁻¹ are shown in **Figure 3a-c**. The capacity of the hv-ZICs increases when illuminated because the photo-generated charges contribute to the measured current, which increases with light intensity (**Figure 3d**). The highest capacity enhancement is observed in the Ag@V₂O₅ hv-ZIC as shown in **Figure 3e** which depicts capacity enhancements ($\frac{C_{ph}-C_d}{C_d} \times 100\%$; where C_d and C_{ph} are gravimetric capacities in dark and illuminated conditions). The capacity enhancement is ~ 35%, ~ 45%, ~

57%, and $\sim 63\%$ for MCNTs@V₂O₅, SCNTs@V₂O₅, pristine V₂O₅, and Ag@V₂O₅ hv-ZICs respectively (scan rate of 100 mV s⁻¹, $\lambda \sim 455$ nm, intensity ~ 12 mW cm⁻²). In addition, CVs using different light wavelengths are shown in **Figure S10**.

The photo-charge mechanism of the Ag@V₂O₅ hv-ZIC can be explained from the energy band diagram of the photoanode shown in **Figure 1a**. We expect that the photo-excited holes move from the photoanode to the AC cathode through the external circuit because of the favorable energy pathways shown in **Figure 1a**, and the unpaired photo-excited electrons will accumulate on the photoanode. This process allows for diffusion of anions to the AC cathode to generate the electrical double layer capacitance and intercalation of cations in the photoanode for photo-charging. Hence, the addition of Ag nanowires to the photoanodes support photo-excited holes transport as well as provide light scattering centers to enhance the overall visible light absorption probabilities (**Figure 2d** and **S4a**). On the other hand, SWCNTs and MWCNTs do not offer favorable photo-excited holes transportation pathways because of energy levels mismatches at the interfaces (see energy band diagrams in **Figure S11**). Further, SWCNTs and MWCNTs absorb some light (as discussed earlier), which further decreases the capacity enhancement as shown in **Figure 3e**. The transport of photo-excited charge carriers through the external circuit is confirmed from the cyclic current response ($I_{ph} - I_d$ at 0 V applied voltage), which increases from 0 $\mu\text{A cm}^{-2}$ to $\sim 60 \mu\text{A cm}^{-2}$ under illumination (for 5 min) and returns to 0 $\mu\text{A cm}^{-2}$ in dark states as shown in **Figure 3f**. These experiments were conducted using a new device which might have suffered from some degradation processes in the initial cycles contributing to the decrease in current observed in **Figure 3f**.

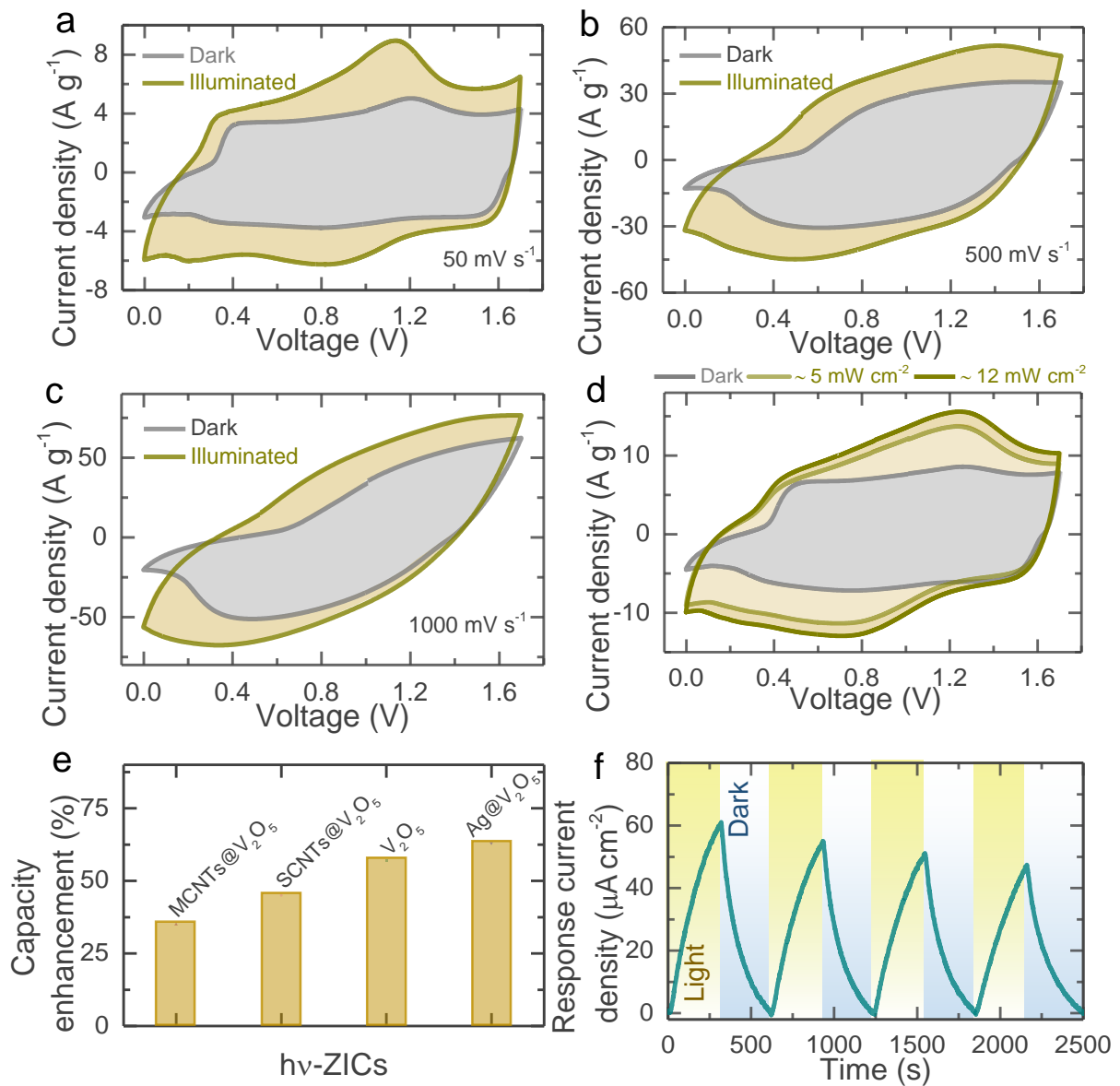


Figure 3. (a-c) CV curves Ag@V₂O₅ hv-ZICs at scan rates of 50 mV s⁻¹, 500 mV s⁻¹ and 1000 mV s⁻¹ in dark and illuminated conditions (λ ~ 455 nm, intensity ~ 12 mW cm⁻²). (d) CVs in dark and illuminated conditions (λ ~ 455 nm) at different light intensities of 5 mW cm⁻² and 12 mW cm⁻² at scan rate of 100 mV s⁻¹. (e) Comparative capacity enhancements of the pristine V₂O₅, SCNTs@V₂O₅, MCNTs@V₂O₅ and Ag@V₂O₅ hv-ZICs at scan rate of 100 mV s⁻¹ under illumination (λ ~ 455 nm, intensity ~ 12 mW cm⁻²). (f) Cyclic absolute response current of the Ag@V₂O₅ hv-ZIC in dark and light illuminated conditions at 0 V applied voltage.

In what follows we investigate the electrochemical performance of Ag@V₂O₅ hv-ZICs in more detail. **Figure 4a,b** shows Galvanostatic charge-discharge (GCD) of Ag@V₂O₅ hv-ZICs both in dark and light ($\lambda \sim 455$ nm, intensity ~ 12 mW cm⁻²), demonstrating clear capacity enhancements when illuminated (e.g. $\sim 74\%$ at 200 mA g⁻¹ and $\sim 51\%$ at 500 mA g⁻¹). Lower current densities allow for longer light interaction and therefore show higher capacity enhancements as summarized in **Figure 4c**. **Figure S12a,b** show the enhancement in capacity and energy density as a function of the current density, which shows an increase in capacity over 40% even at high current densities of 2000 mA g⁻¹. Further, this value increases with increasing light intensity (**Figure S12c**). Finally, we calculate the energy density and power density of Ag@V₂O₅ hv-ZICs under illumination, which are ranging from 32.45 Wh kg⁻¹ to 53.13 Wh kg⁻¹ at 1384.61 W kg⁻¹ to 36.74 W kg⁻¹. The Ragone plot in **Figure 4d** shows that in addition to offering light charging capabilities, the performance of this capacitor is comparable with state of the art asymmetric supercapacitors (AC vs metal oxides/hydroxides/sulfides electrodes).

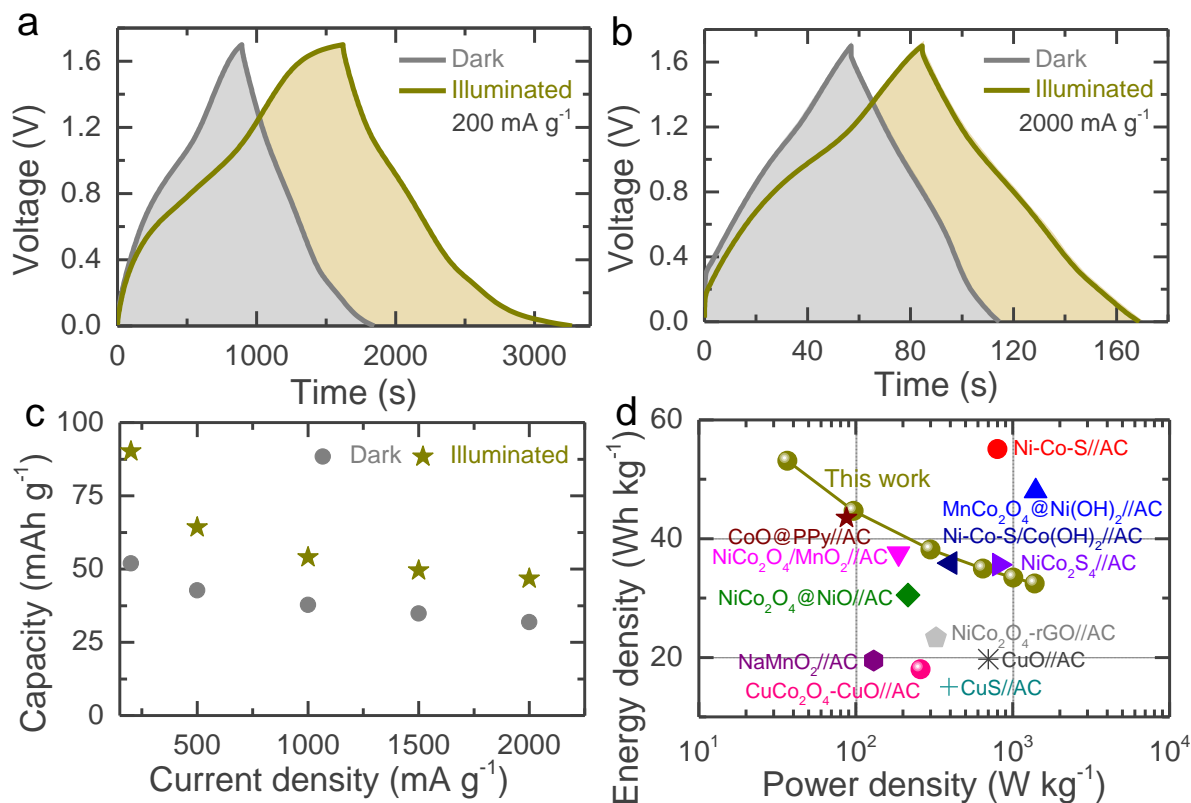


Figure 4. (a,b) GCDs of the Ag@V₂O₅ hv-ZIC at current densities of 200 mA g⁻¹ and 2000 mA g⁻¹ in dark and illuminated ($\lambda \sim 455$ nm, intensity ~ 12 mW cm⁻²) conditions. (c) Capacity with respect to current density plot of the Ag@V₂O₅ hv-ZIC in dark and illuminated. (d) Ragone plot shows the comparison of energy density and power density of our Ag@V₂O₅ hv-ZIC with those reported for asymmetric supercapacitors in literature: CuS//AC,³⁶ CuCo₂O₄-CuO//AC,³⁷ CuO//AC,³⁸ NaMnO₂//AC,³⁹ NiCo₂O₄-rGO//AC,⁴⁰ NiCo₂O₄@NiO//AC,⁴¹ NiCo₂O₄/MnO₂//AC,⁴² Ni-Co-S/Co(OH)₂//AC,⁴³ CoO@PPy//AC,⁴⁴ NiCo₂S₄//AC,⁴⁵ MnCo₂O₄@Ni(OH)₂//AC,⁴⁶ Ni-Co-S//AC,⁴⁷ etc .

Impedance spectra in dark and illuminated conditions ($\lambda \sim 455$ nm, intensity ~ 12 mW cm⁻²), in **Figure 5a** show that the series resistance of our Ag@V₂O₅ hv-ZICs remains similar when illuminated (decreases from ~ 2.9 Ω to ~ 2.35 Ω), whereas the charge transfer resistance decreases from ~ 25 Ω to ~ 9.5 Ω . This is in agreement with a reduction in impedance measured

in the I-V profiles of Ag@V₂O₅ when illuminated as shown in **Figure 2a**. The equivalent circuit of the Ag@V₂O₅ hv-ZICs in dark and illuminated conditions is shown in **Figure S13**. To study the long-term capacity retention of the Ag@V₂O₅ hv-ZIC, we measure CVs and GCDs for 500 cycles in dark and illuminated conditions. **Figure 5b** shows the 1st, 50th, 250th and 500th CV curve at a scan rate of 200 mV s⁻¹ in illuminated conditions ($\lambda \sim 455$ nm, intensity ~ 12 mW cm⁻²). There is no significant change in the CV profiles after 500 CV cycles. **Figure 5c,d** shows 4000 GCD cycles of the Ag@V₂O₅ hv-ZICs in dark and light conditions at a current density of 1000 mA g⁻¹. The Ag@V₂O₅ hv-ZICs achieve a capacity retention of $\sim 99\%$ after 4000 cycles in dark conditions and high coulombic efficiencies ($\sim 100\%$ after 4000 cycles). When illuminated the capacity measured by GCD increases slightly over the 4000 cycles, which is probably related to the capacity increase seen in the CVs over time close to 0V (**Figure 5b**). These results further confirm the stability of the Ag@V₂O₅ hv-ZICs both in dark and illuminated conditions.

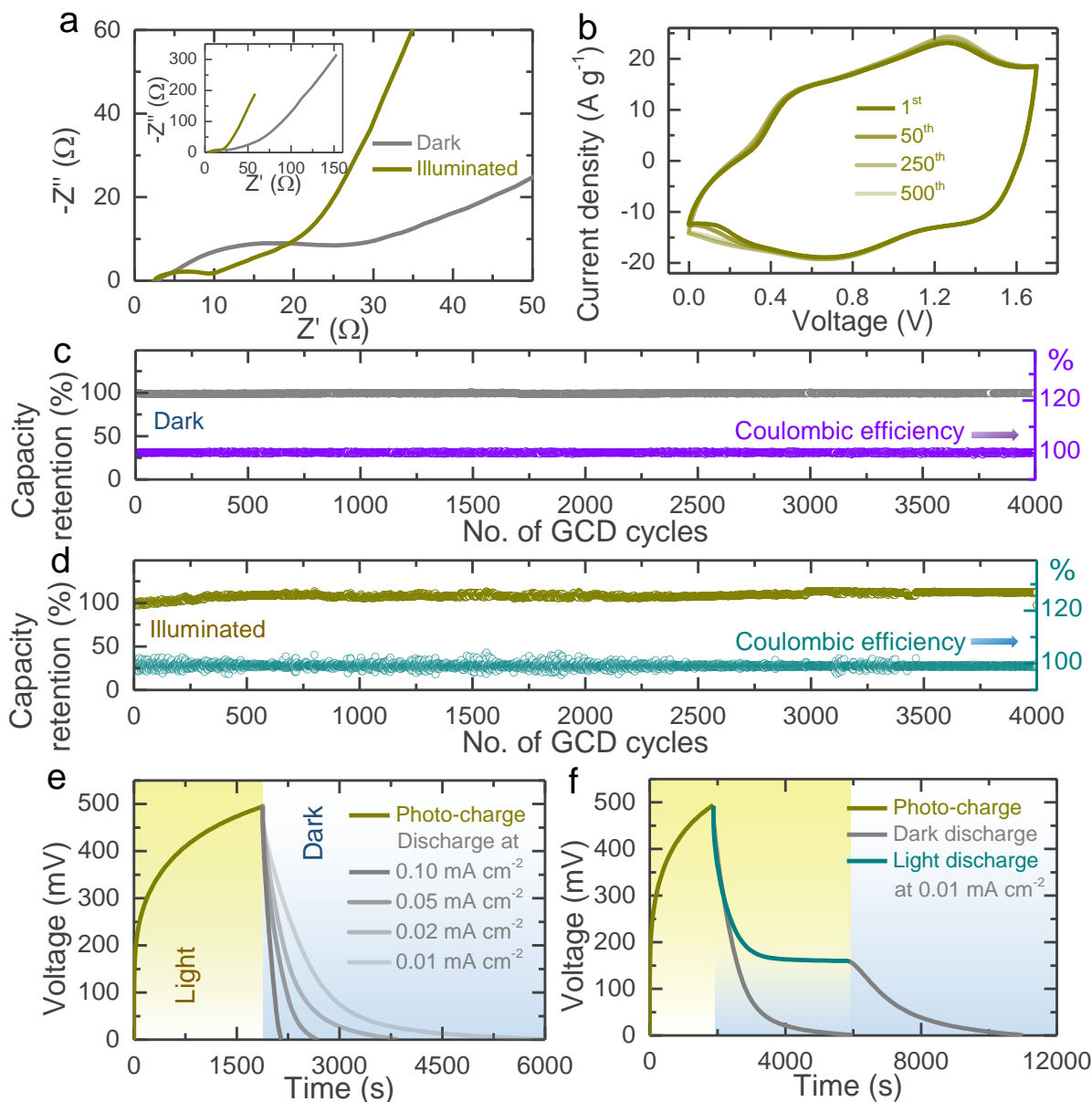


Figure 5. (a) AC impedance of the Ag@V₂O₅ hv-ZIC in dark and illuminated conditions ($\lambda \sim 455$ nm, intensity ~ 12 mW cm⁻²) acquired in the frequency range of 10 mHz to 100 kHz at amplitude of 10 mV. (b) 1st, 50th, 250th and 500th CV cycles of illuminated Ag@V₂O₅ hv-ZICs ($\lambda \sim 455$ nm, intensity ~ 12 mW cm⁻², scan rate of 200 mV s⁻¹) (c,d) Capacity retentions and coulombic efficiencies over 4000 GCD cycles at 1000 mA g⁻¹ of the Ag@V₂O₅ hv-ZICs both in dark and light ($\lambda \sim 455$ nm, intensity ~ 12 mW cm⁻²). (e) Photo-charge ($\lambda \sim 455$ nm, intensity ~ 12 mW cm⁻²) and discharge at different current densities (0.1 to 0.01 mA cm⁻²). (f) Discharges at 0.01 mA cm⁻² in dark and illuminated conditions of photo-charged Ag@V₂O₅ hv-ZICs.

The above experiments show how light influences CV and GCD curves, in what follows, we measure the charging of Ag@V₂O₅ hv-ZIC by light without applying any external current or voltage. **Figure 5e** shows the photo-charging curve, which takes about 30 min to reach 500 mV ($\lambda \sim 455$ nm, intensity ~ 12 mW cm⁻²). At the discharge current densities of 0.1 mA cm⁻² and 0.01 mA cm⁻², the measured photo-charged energy densities are ~ 1.67 μ Wh cm⁻² at ~ 48 mF cm⁻² and ~ 2.9 μ Wh cm⁻² at ~ 83 mF cm⁻², respectively. The photo-charged hv-ZIC are then discharged at different current densities (**Figure 5e**). It is important to note that the Ag@V₂O₅ hv-ZIC can be charged by light while delivering a load as shown in **Figure 5f**. Photo-charged Ag@V₂O₅ hv-ZICs discharge slower under illumination than in dark conditions, which is because the capacitor is recharged by light whilst at the same time being discharged galvanostatically. In these experiments, the device voltage output decreases until the current generated by the photo-charging process is equal to the discharge current. In the conditions used in this particular experiment, (discharge current density of 0.01 mA cm⁻² and ~ 12 mW cm⁻² illumination with $\lambda \sim 455$ nm), this equilibrium is reached at an output voltage of 160 mV (See **Figure 5f**). Once the light source is turned off, the Ag@V₂O₅ hv-ZIC discharges to 0 V as expected. Based on the photo-charging response, we calculate the photo conversion efficiency of our Ag@V₂O₅ hv-ZIC, which is $\sim 0.05\%$. The photo conversion efficiency these hv-ZICs are nearly five times higher than that of the graphitic carbon nitride light rechargeable electrochemical capacitors.²⁵ In addition, The photo-charge energy density is improved from 0.7 to 4.8 Wh kg⁻¹ and the capacity from 11.4 to 138 F g⁻¹ compared to previous hv-ZICs.²⁵

Overall, this report presents a photo-capacitor that can simultaneously harvest and store optical energy without the need of any solar cell or external circuitry. This is made possible by the internal photo-charge carriers' separation and transportation in our Ag@V₂O₅ electrodes. These devices outperform previously reported photo-capacitor, and achieve energy densities

of $\sim 53 \text{ Wh kg}^{-1}$ which is comparable to the best reported asymmetric supercapacitors. Finally, these devices achieve a capacity retention of 99% over 4000 cycles.

EXPERIMENTAL SECTION

Material Synthesis and Characterizations. V_2O_5 nanofibers were synthesized by a hydrothermal process.^[26] First, 0.364 g V_2O_5 powder (Sigma-Aldrich) is mixed with 30 mL de-ionized water under stirring ($\sim 300 \text{ rpm}$) at room temperature for 30 min. Then, 5 mL of 30% H_2O_2 added into the solution and continued stirring for another 30 min. The resultant transparent orange solution was transferred into a $\sim 40 \text{ mL}$ autoclave and then placed in an oven to maintain at 205°C for two days. The product was washed with de-ionized water and ethanol followed by alternative centrifugation and finally annealed at $\sim 400^\circ\text{C}$ for 1 h in air. **Figure S14** shows SEM, EDS, XRD and Raman spectroscopy of the source material i.e. V_2O_5 powder used for the synthesis of V_2O_5 nanofibers.

The SCNTs, MCNTs and Ag nanowires are received from Sigma, Nanocyl and Sigma-Aldrich, which are used without further purification.

The samples were characterized by SEM (FEI Magellan 400L with an acceleration voltage of 5 kV), TEM equipped with an X-ray EDS (Talos F200X G2 with an acceleration voltage of 200 kV), XRD (Bruker D8 Advance, $\text{Cu K}\alpha$ radiation), Raman spectroscopy (Renishaw InVia), and optical absorbance/transmission (PerkinElmer UV/VIS/NIR Spectrometer (Lambda 750)).

Preparation of Photo-electrodes. First, 94.8 mg V_2O_5 nanofibers and 0.2 mg Ag nanowires were dispersed in 2 mL N-Methyl-2-pyrrolidone (NMP, Sigma-Aldrich) using mixing (VWR Analog Vortex Mister) and ultra-sonication. Then, 5 mg polyvinylidene fluoride (PVDF, Solef 6020) binder added into solution to prepare the $\text{Ag@V}_2\text{O}_5$ electrode solution. Similarly, the other SCNTs@ V_2O_5 and MCNTs@ V_2O_5 electrode solutions are prepared by adding 0.2 mg SCNTs and 0.2 mg MCNTs with 94.8 mg V_2O_5 and 5 mg PVDF binder followed by same

procedure. Finally, the photoelectrodes are obtained by drop casting electrodes solutions on FTO coated glass substrates (received from Sigma-Aldrich, surface resistivity $\sim 7 \text{ } \Omega\text{sq}^{-1}$) followed by drying at $\sim 120 \text{ } ^\circ\text{C}$ in vacuum oven.

Designing of hv-ZICs. The coin cell (CR2450) type hv-ZIC is designed followed by making a hole ($\sim 8 \text{ mm}$ diameter) on coin cell for an optical window. The photoanode is placed on the optical window side and fixed using EPOXY (EVO-STIK) to allow for light illumination. The Zn strip (Alfa Aesar, 0.25 mm thick) was used for electrical connection between photoanode and coin cell. The Whatman glass microfiber filters paper separator is placed and added $\sim 150 \text{ } \mu\text{L}$ of $3 \text{ M Zn}(\text{CF}_3\text{SO}_3)_2$ (Sigma-Aldrich) aqueous electrolyte. Thereafter, the AC cathode is placed on top of the separator and finally assembled followed by placing the stainless steel disk and spacer.

Electrochemical Testing of the hv-ZICs. CVs at different scan rates and GCDs at different current densities in dark and illuminated conditions of the hv-ZICs are measured by using a Biologic VMP-3 galvanostat. Different light wavelengths of 455 nm , 470 nm , 528 nm , and white were used to test photo-charging response of the hv-ZICs. The AC impedance test of the hv-ZIC is measured in the frequency range (10 mHz to 100 kHz) in dark and illuminated ($\lambda \sim 455 \text{ nm}$, intensity $\sim 12 \text{ mW cm}^{-2}$). The photo-charge measurements of the hv-ZIC are acquired by measuring the open circuit voltage, and recorded the discharge responses at different applied current densities.

Fabrication of Photodetectors and Electrical Measurements. For electrical photoresponse measurements, the photodetectors are fabricated by direct drop casting V_2O_5 , SCNTs@ V_2O_5 , MCNTs@ V_2O_5 and Ag@ V_2O_5 materials on Gold (Au, 40 nm)/Chromium (Cr, 10 nm) IDEs patterned on $\text{Si}_3\text{N}_4/\text{Si}$ wafer followed by standard UV lithographic technique. The current-voltage responses of the photodetectors are recorded in voltage range (-2 V to $+2 \text{ V}$) in dark

and illuminated ($\lambda \sim 455$ nm) using Agilent Sourcemeter integrated to Suss MicroTec Probe Station. Moreover, the cyclic current-time responses of the photodetectors are recorded under periodic light illumination at 1 V applied bias voltage.

Time Correlated Single Photon Counting. The carriers' lifetime of the sample was extracted using a biexponential decay model. The pulsed diode laser of 407 nm wavelength was used as an excitation source. The blue laser (407 nm) was driven using DH400, PicoQuant laser controller and generates pulses with 80 ps full width at half maximum (FWHM). This time-correlated single photon counting (TCSPC) setup encompasses of a monochromator coupled with a micro channel plate photomultiplier tube (MCP-PMT from Hamamatsu - R3809U-50) and TCSPC electronics (Lifespec-pc and VTC900 PC card from Edinburgh Instruments).

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website

Raman of nanofibers (Figure S1), SEM images of SCNTs, MCNTs and Ag nanowires (Figure S2); IV profiles of the pristine V_2O_5 , SCNTs@ V_2O_5 and MCNTs@ V_2O_5 photodetectors (Figure S3); Absorbance and steady state PL spectra of the samples (Figure S4); SEM images of the photoanodes (Figure S5); Cross-section SEM image (Figure S6); Digital photograph of optical coin cell and SEM image of AC (Figure S7); Capacity plot at different anode to cathode mass ratios (Figure S8); CV curves of the hv-ZICs in dark and illuminated (Figures S9 and S10); Energy band diagrams of the hv-ZICs (Figure S11); Capacity enhancement, energy density and capacity plots of the Ag@ V_2O_5 hv-ZIC (Figure S12); Equivalent circuit of AC impedance results (Figure S13); SEM, EDS, Raman and XRD of the commercial V_2O_5 particles (Figure S14).

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Notes

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