Photo-Enhanced Magnesium-Ion Capacitors Using Photoactive Electrodes

*Sul Ki Park, Buddha Deka Boruah, Arvind Pujari, Byung-Man Kim, and Michael De Volder**

Off-grid power sources are becoming increasingly important for applications ranging from autonomous sensor networks to fighting energy poverty. Interactions of light with certain classes of battery and capacitor materials have recently gained attention to enhance the rate performance or to even charge energy storage devices directly with light. Interestingly, these devices have the potential to reduce the volume and cost of autonomous power sources. Here, a light-enhanced magnesium (Mg)-ion capacitor is shown. The latter is interesting because of the large natural abundance of Mg and its ability to operate in low cost and non-flammable aqueous electrolytes. Photoelectrodes using a combination of vanadium dioxide and reduced graphene oxide can achieve capacitance enhancements of up to 56% under light exposure alongside a 21% higher energy density of 20.5 mAh kg^{-1}.

1. Introduction

The study of light–matter interactions in certain types of capacitor and battery materials (i.e., photo-enhanced energy storage systems) has recently gained attention because light can enhance the performance of electrochemical energy storage systems in a number of interesting ways, such as increasing capacities, faster charging rates or even charging with light only. To develop attractive light enhanced batteries and capacitors, researchers have been looking into materials with both active optical and electrochemical properties such that harvesting and storing solar energy is possible in the same material and components. The concept of enhancing the performance of energy storage devices by light has been demonstrated in Li-ion batteries,[1–5] Zn-ion batteries[6] and capacitors,[7] Redox Flow batteries,[8] and Li-air batteries.[9–11]

Recently, magnesium (Mg)-ion batteries and capacitors have been studied because of the natural abundance of Mg, limited dendrite formation when plating and stripping Mg metal and high chemical stability against moisture and oxygen.[12–15] In addition, Mg offers high theoretical gravimetric (2205 mAh g^{-1}) and volumetric (3833 mAh cm^{-3}) capacities because it is divalent.[13,15] However, compared to monovalent ions such a Li, the kinetics of Mg based systems tend to be sluggish.

To the best of our knowledge, this work reports the first photo-enhanced Mg-ion capacitor and demonstrate that light can improve the capacitances and rate performance of these devices. In this study, vanadium dioxide (VO_2) was selected as a photo-active electrode material that drives light enhancement and at the same time stores charges. It was paired with an activated carbon (AC) counter electrode (**Figure 1**a) to create devices we will refer to as Photo-enhanced Mg-Ion Capacitors (Photo-MICs). The asymmetric electrode design used in this work (VO_2 and AC) allows to increase the operating potential of the device, in this case to 1.8 V.[16] VO_2 is selected both because of its bandgap (≈2.3 eV) which is suitable for light harvesting and its framework like structure with large tunnels of ≈0.82 and ≈0.5 nm^2 along *b*-axis and *c*-axis that allow for a direct pathway for effective insertion/extraction of Mg-ions.[13,14,17–19]

Figure 1a depicts the energy diagram of the photo-electrodes proposed in this paper, which is designed such that it facilities the extraction of electrons from VO_2. Light exposure of our Photo-MICs resulted in an enhancement of capacitance with up to 56% at high current densities alongside a 21% higher energy density (light wavelength $\lambda \approx 455$ nm and intensity ≈12 mW cm^{-2}). In addition, we observed a good cycling stability in both light and dark conditions.

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DOI: 10.1002/smll.202202785

2. Results and Discussion

The VO_2 nanorods used in these devices are synthesized using a hydrothermal process. Shortly, ammonium metavanadate (2.0 g) and oxalic acid (3.75 g) were dissolved into deionized water (120 mL) and heated to 180 °C for 12 h in an autoclave (see details in the Experimental Section). Figure 1b shows a scanning electron microscope (SEM) image of the as-synthesized VO_2 nanorods alongside XRD patterns (Figure 1c) assigned to VO_2(B) (JCPDS. No. 65-7960) phase.[20] The Brunauer–Emmett–Teller (BET) N_2 adsorption/desorption isotherms show that the specific surface area of the VO_2 is around 29.07 $m^2\ g^{-1}$ (Figure S1, Supporting Information). Finally, Figure 1d shows a UV–vis spectrum confirming the bandgap of the material is ≈2.3 eV as reported previously.

The photoelectrodes are prepared by mixing the VO_2 nanorods described above with reduced graphene oxide (rGO) and a polyvinylidene fluoride (PVDF) in a mass ratio of 90:5:5 and are casted on carbon felt (CF) collector electrodes (see Experimental Section for more details). The addition of rGO in the photocathode can help with separation and transportation of photo-generated electrons to the counter electrode through a favorable energy pathway, as illustrated in Figure 1a.[6]

Before building photo-MICs, we investigated the photosensitivity and the separation of photo-excited charge in proposed photocathode, a photodetector (PD) was fabricated. Details of the PD fabrication and a schematic of the devices are provided in the Experimental Section. **Figure 2**a shows the current (*I*)–voltage (*V*) curves in dark and light conditions for a PD, where VO_2/rGO was cast on fluorine-doped tin oxide (FTO) and connected with silver (Ag). The current output of the PD increases when exposed to light ($\lambda \approx 455$ nm) because of photocharge separation in the VO_2/rGO heterojunction (Figure 2a). In addition, Figure 2a shows that at 0 V bias, the current is almost 0 under dark conditions and is positive when light is applied. The photocurrent measurement at 0 V is also confirmed by a current (*I*)–time (*t*) curve provided in Figure 2c, which shows a photocurrent of ≈5.0 µA is generated under illumination. It indicates that charge separation is possible even under no bias voltage at 0 V. The current (*I*)–time (*t*) curve in light and dark conditions at a bias voltage of 1 V shows a similar enhancement of photocurrent (see Figure 2d). These results indicate that a stacked photocathode of FTO/rGO/VO_2/Ag is able to generate and separate photo-generated electron/hole pairs. We think this process is driven by the energy band diagram shown in Figure 2e, where photo-generated electrons are transported through rGO to FTO and holes are predominantly transported to the silver contact. In addition, the response current of a photo-MIC was measured under light and dark conditions at an applied voltage equal to the open circuit voltage (OCV) (Figure 2f). This experiment shows the response current increases from 5.7 to 12 µA in the photo-MIC when the light is turned on as a result of the light generated charge carriers. In this stage, Mg^{2+} and NO_3^- ions move easily toward AC and photocathode, respectively (Figure 1a).

To study these effects of light exposure, cyclic voltammetry (CV) of the Photo-MIC was measured in dark and light conditions ($\lambda \approx 455$ nm, intensity ≈12 mW cm^{-2}) between 0 and 1.8 V. **Figure 3**a–d and Figure S2 (Supporting Information) show these CVs at scan rates ranging from 25 to 1000 mV s^{-1}. The CV curves recorded in our devices show a pseudo-capacitive behavior with distinct redox reaction peaks

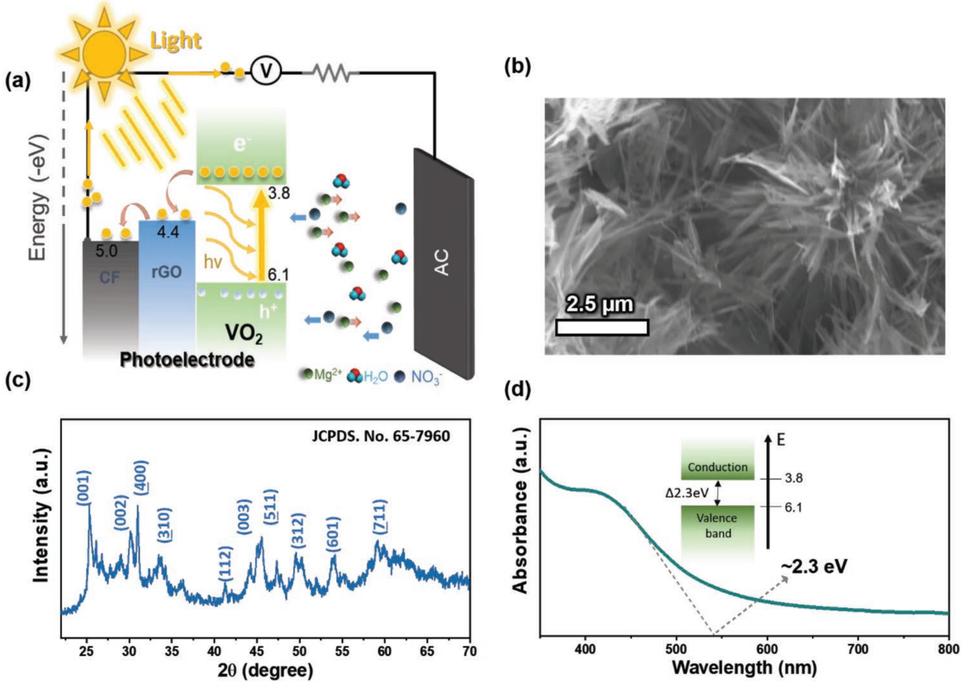

Figure 1. a) Schematic illustration of the photocharging process of Photo-MIC using VO_2/rGO photo electrode and AC counter electrode. b) SEM image of hydrothermally synthesized VO_2 used in this work, c) XRD pattern, and d) UV–vis absorption spectrum of the VO_2 nanorods synthesized in this work.

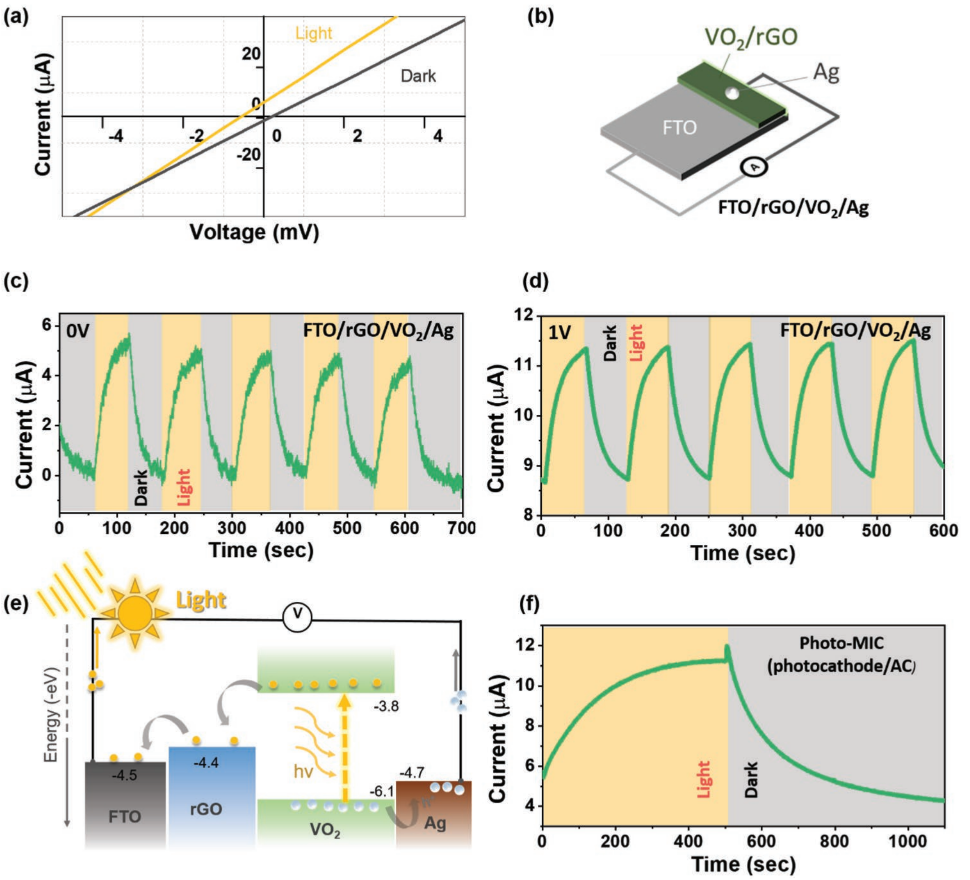

Figure 2. a) Current (*I*)–voltage (*V*) curves of a PD using FTO/rGO/VO$_2$/Ag in dark and light conditions ($\lambda \approx 455$ nm). b) The illustration of PD using FTO/rGO/VO$_2$/Ag. c,d) Current (*I*)–time (*t*) measurements of a PD using FTO/rGO/VO$_2$/Ag in dark and light conditions at an external bias voltage at 0 and 1 V, respectively. e) Energy band diagram of a PD design. f) The response current plot of the photo-MIC at an applied voltage equal to OCV.

during charging and discharging, which corresponds to the following reactions for (1) VO$_2$ on the photo-electrode side:[]

$$VO_2 + x \cdot Mg^{2+} + 2x \cdot e^- \leftrightarrow Mg_x \cdot VO_2 \tag{1}$$

During discharging, Mg ions are inserted in VO$_2$ (VO$_2$ to Mg$_x$VO$_2$) and[18,19] on the AC as a counter electrode charges are stored in the double layer on the surface of AC.[18,19] In the charge process, the pseudo-peaks correspond to the Mg removal from Mg$_x$VO$_2$.[18,19]

The measured current (and hence the area of the CV curves) increased under illumination, which indicates an improvement in capacitance. The method of calculating the capacitance is shown in Figure S2 (Supporting Information). As illustrated in Figure 3e, the capacitance increases by 30.0%, 24.2%, 23.6%, 22.3%, 17.9%, and 14.2% at scan rates of 25, 75, 200, 300, 500, and 1000 mV s^{-1} under illumination (improvement calculated as $(C_{ph}-C_d)/C_d \times 100\%$, with C_d and C_{ph} the gravimetric capacitances in dark and illuminated conditions). The higher capacitance enhancements at slow scan rate can be explained by a longer light exposure under these conditions and therefore more photocharges contributing to the output current, as suggested in earlier reports.[7]

Galvanostatic charge–discharge (GCD) curves of the Photo-MIC were measured under dark and light conditions using specific current densities ranging from 0.65 to 16.2 A g^{-1}. **Figure 4**a,b, Figure S3 and Table S1 (Supporting Information) clearly show enhancements in capacitance when the devices are illuminated as expected from the CV responses (the capacitances were calculated based on the mass of both electrodes). The capacitances increase from 51.38 to 63.80 F g^{-1} (24% enhancement at 0.65 A g^{-1}) and from 19.26 to 30.12 F g^{-1} (56% at higher 16.2 A g^{-1} current densities). The specific capacitances of electrodes were calculated using the following equation:

$$C = I/(m \cdot V/t) \tag{2}$$

where C is the specific capacitance of the electrode (F g^{-1}), m is the mass of the active electrode (g), I is the current (A), V is the voltage (V), and t is the discharge time. The V/t term corresponds to the slope obtained from the discharge curve in GCD.

Figure 4c summarizes the capacitances measured at different current densities in light and dark conditions and shows how under illumination, a better capacitance retention is achieved at high current density. In other words, light not only improves the capacitance but also the rate

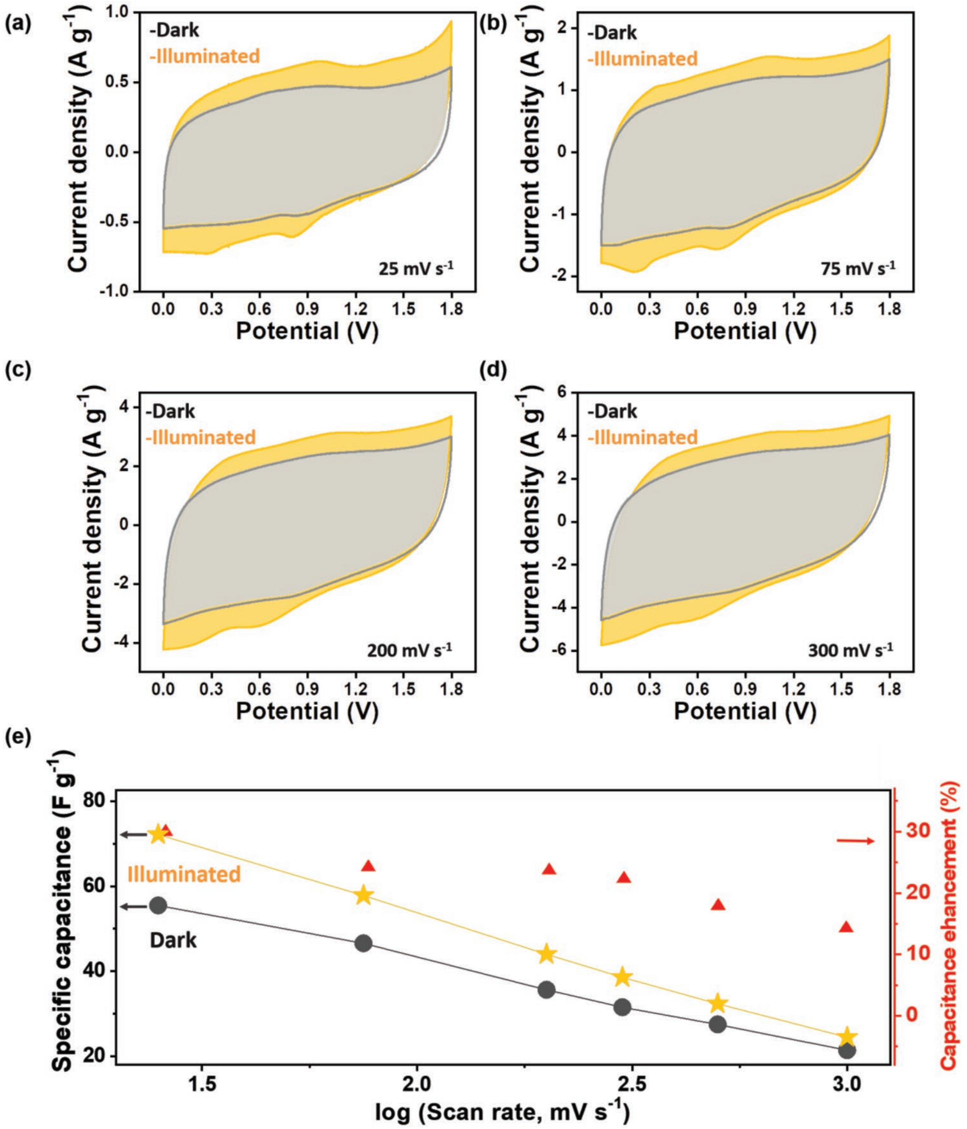

Figure 3. CV measurements of Photo-MICs in dark and light conditions ($\lambda \approx 455$ nm and intensity ≈ 12 mW cm^{-2}) at varying scan rates of a) 25 mV s^{-1}, b) 75 mV s^{-1}, c) 200 mV s^{-1}, and d) 300 mV s^{-1}. e) Capacitance enhancement of Photo-MIC under light as a function of the scan rate.

capability (i.e., the capacitance at 16.2 A g^{-1} divided by the capacitance 0.65 A g^{-1}) from 37.5% to 47.2%, under dark and light, respectively. This improvement in rate capability could be related to the reduction in impedance of the electrode under illumination as observed by electrochemical impedance spectroscopy (EIS) tests shown in Figure 4d. Figure 4d shows that the charge transfer resistance (R_{ct}) decreases from 0.69 to 0.20 Ω when exposed to light, which may be due to additional photo-generated charges taking part in the operation of the device.[21,22]As shown in Figure S4 (Supporting Information), we also found that illuminating a discharged Photo-MICs leads to an increase in their output voltage from 0 to 0.07 V ($\lambda \approx 455$ nm, intensity ≈12 mW cm^{-2} for 30 min), which is a first step toward achieving photo-charging. Overall, the devices achieved a higher energy density of 20.5 mAh kg^{-1} when illuminated (based on the mass of two electrodes). In addition, the cycling stability was investigated in dark and light conditions at a current density of 0.5 A g^{-1} (Figure 4e and Figure S5a, Supporting Information). Figure S5a (Supporting Information) shows a capacitance retention of 77.0% over 1400 cycles in dark conditions. To test the stability under illumination, we first test a cell for 375 cycles in dark conditions and found a capacitance retention of 82.5% (Figure 4e). We then turned our light source on, resulting in a capacitance increase as expected from our photo-cathodes. Figure 4e shows a capacitance retention of 82.6% during the following ≈400 cycles under illumination. As a side note, we observe that the after turning the light on, the capacitance reaches a maximum after 3–5 cycles, which is also reflected in the device charge transfer resistance that gradually decreases over the first 3 cycles (see EIS data in Figure S5b, Supporting Information).

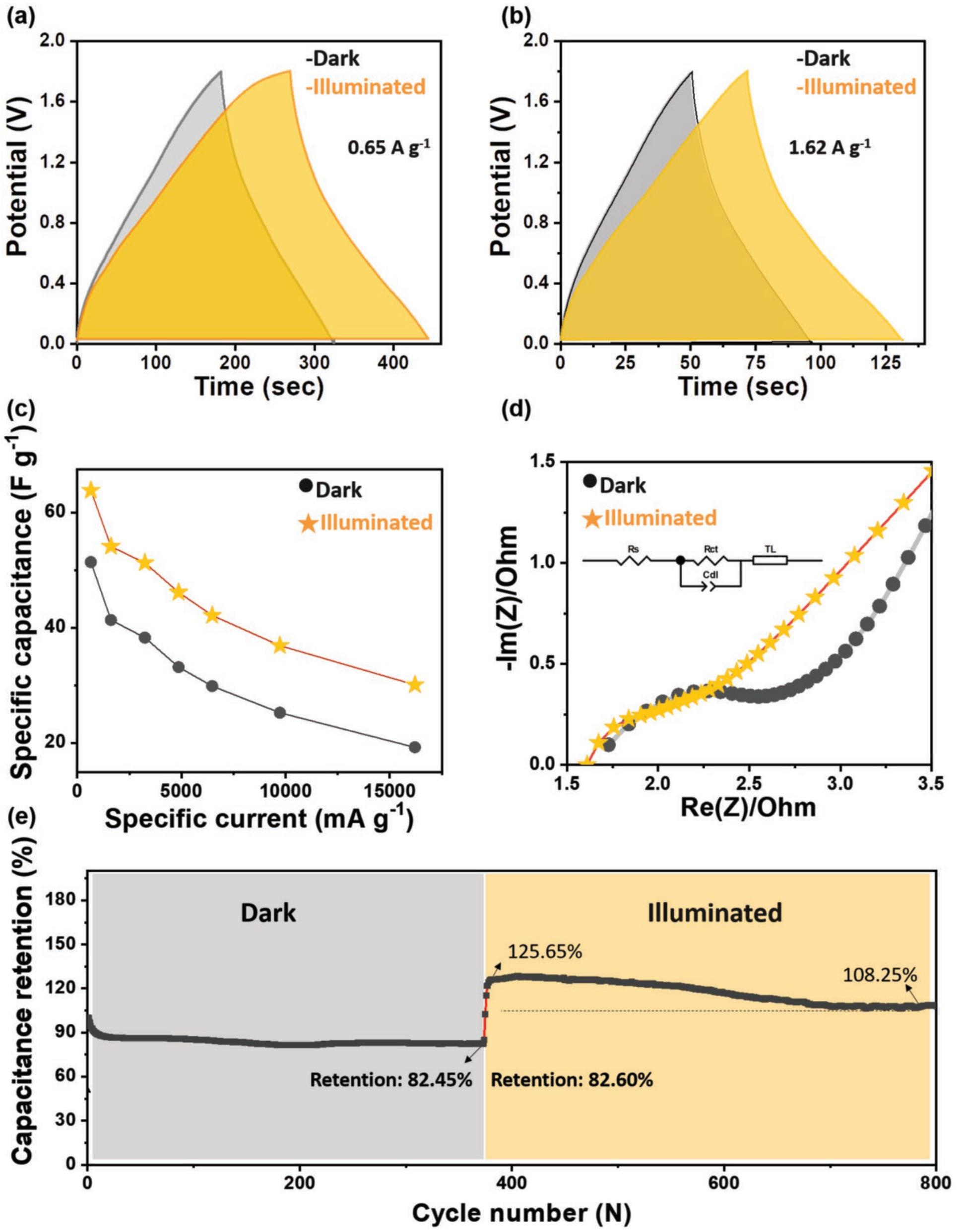

Figure 4. Galvanostatic measurements under dark and illuminated conditions ($\lambda \approx 455$ nm, intensity ≈ 12 mW cm^{-2}) of Photo-MICs at specific currents of a) 0.65 A g^{-1} and b) 1.62 A g^{-1}. c) Rate capability test of Photo-MICs under dark and illuminated conditions. d) EIS test of Photo-MIC in the frequency range from 10 mHz to 100 kHz at 10 mV amplitude under dark and illuminated conditions. e) Cycle stability test of Photo-MIC at 0.5 A g^{-1} under dark and illuminated conditions.

3. Conclusions

Mg-ion based devices are interesting because of the natural abundance of Mg, limited dendrite formation when plating and stripping Mg metal and gravimetric and volumetric capacitance. However, Mg-ion based systems tend to have slow kinetics and in this work, we show that light can be used to increase the capacitance and rate performance when using photo-cathodes that consist of a mixture of VO_2 and rGO to generate and separate photo charges. We found that under illumination, the capacitance of our devices increases with up to 56% at high current densities. In addition, we also investigate the cycling stability of these photo-enhanced capacitors and found a capacitance retention of 77.0% over 1400 cycles in dark conditions and 82.6% over 400 cycles in light conditions.

4. Experimental Section

Material Synthesis and Photoelectrode Preparation: First, ammonium metavanadate (2.0 g) and oxalic acid (3.75 g) dissolved into deionized water (120 mL) followed by stirring for 12 h at room temperature. Then, the growth was transferred into an autoclave reactor and then maintained at 180 °C for 12 h. Thereafter, the suspension was cleaned with deionized water/ethanol followed by centrifugation process. Finally, samples were obtained by drying at ≈120 °C for 12 h in a vacuum oven.

For photoelectrode preparation, 91 mg VO_2 and 4 mg rGO dispersed in 4 mL *N*-Methyl-2-pyrrolidone (NMP, Sigma-Aldrich) using sonication. Then, 5 mg PVDF (Solef 6020) binder was added. As obtained photocathode solution was dropcasted on CF (Sigracet GDL 39 AA carbon graphite paper, SGL Carbon) current collectors and dried at 120 °C in vacuum oven.

Material Characterization: Morphologies of VO_2 materials were observed by scanning electron microscopy (SEM, a GEMINI 1530VP FEG-SEM system). X-ray diffraction (XRD) patterns were obtained by using a Bruker D8 Advance (Cu K_α radiation, 6° min^{-1} scan). Moreover, the optical properties of the samples were characterized by using UV/vis/NIR Spectrometer (Perkin Elmer, Lamda 750). BET surface area characterizations are employed using Micromeritics 3Flex (under nitrogen environment).

Design of Photodetector (PD) and Measurements: As-prepared VO_2/rGO dispersion was dropcasted on the FTO coated glass and dried at 120 °C. Then, silver (Ag) was pasted on the dried surface of VO_2/rGO. *I–V* measurements were conducted from −1 to 1 V in dark and light conditions using a Kiethely B2901A source meter. *I–t* measurements were conducted by switching dark and light conditions every 60 s at an external bias voltage ($V = 0$ and 1 V).

Design of Photo-MICs: Coin cell (CR2450) type Photo-MICs designed by making a ≈8 mm hole on coin cell case and sealed with a glass window for illumination. The photoelectrode is placed on the side of the coin cell having the optical window and connected photoelectrode with coin cell using carbon nanotubes strip for electrical connectivity. Finally, a Whatman glass microfiber filters paper separator, ≈200 µL of 1 м $Mg(NO_3)_2$ (Sigma-Aldrich) aqueous electrolyte with activated carbon as a counter electrode were used to obtain the Photo-MIC. The mass loading of photocathode and AC are 0.81 and 2.44 mg cm^{-2}, respectively.

Electrochemical Tests: CV curves at different scans range from 25 to 1000 mV s^{-1} over working voltage range of 0 and 1.8 V were tested by using a Biologic VMP-3 galvanostat in dark and illuminated (light source $\lambda \approx 455$ nm, intensity ≈ 12 mW cm^{-2}). Likewise, galvanostatic discharge–charge measurements were extended at different specific currents range from 648 to 16200 mA g^{-1} in in dark and illuminated conditions. AC impedance (EIS) measurements of the Photo-MIC tested in the frequency range from 10 mHz to 100 kHz at 10 mV voltage amplitude in dark and illuminated states. Furthermore, the photocharging measurements were employed by recording open circuit voltage response (in absence of external current under light illumination) and discharged them by applying specific currents.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

S.K.P. and B.D.B. contributed equally to this work. This project was supported by funding from an ERC Consolidator Grant MIGHTY – 866005, as well as the EPSRC project EP/T015233/1 and NanoDTC Cambridge EP/S022953/1.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

light-enhanced capacitors, magnesium-ion capacitors, photoactive electrodes, VO_2

Received: May 5, 2022
Revised: July 26, 2022

[1] N. Tewari, S. B. Shivarudraiah, J. E. Halpert, *Nano Lett.* **2021**, *21*, 5578.
[2] S. Ahmad, C. George, D. J. Beesley, J. J. Baumberg, M. De Volder, *Nano Lett.* **2018**, *18*, 1856.
[3] K. Kato, A. B. Puthirath, A. Mojibpour, M. Miroshnikov, S. Satapathy, N. K. Thangavel, K. Mahankali, L. Dong, L. M. R. Arava, G. John, *Nano Lett.* **2021**, *21*, 907.
[4] A. Lee, M. Vörös, W. M. Dose, J. Niklas, O. Poluektov, R. D. Schaller, H. Iddir, V. A. Maroni, E. Lee, B. Ingram, *Nat. Commun.* **2019**, *10*, 1784.
[5] A. Paolella, C. Faure, G. Bertoni, S. Marras, A. Guerfi, A. Darwiche, P. Hovington, B. Commarieu, Z. Wang, M. Prato, *Nat. Commun.* **2017**, *8*, 14643.
[6] B. Deka Boruah, A. Mathieson, S. K. Park, X. Zhang, B. Wen, L. Tan, A. Boies, M. De Volder, *Adv. Energy Mater.* **2021**, *11*, 2100115.
[7] B. Deka Boruah, A. Mathieson, B. Wen, C. Jo, F. Deschler, M. De Volder, *Nano Lett.* **2020**, *20*, 5967.
[8] N. Yan, G. Li, X. Gao, *J. Mater. Chem. A* **2013**, *1*, 7012.
[9] Y. Liu, N. Li, S. Wu, K. Liao, K. Zhu, J. Yi, H. Zhou, *Energy Environ. Sci.* **2015**, *8*, 2664.
[10] Y. Liu, N. Li, K. Liao, Q. Li, M. Ishida, H. Zhou, *J. Mater. Chem. A* **2016**, *4*, 12411.
[11] Q. Lv, Z. Zhu, S. Zhao, L. Wang, Q. Zhao, F. Li, L. A. Archer, J. Chen, *J. Am. Chem. Soc.* **2021**, *143*, 1941.
[12] K. V. Kravchyk, M. Walter, M. V. Kovalenko, *Commun. Chem.* **2019**, *2*, 84.
[13] C. Pei, F. Xiong, J. Sheng, Y. Yin, S. Tan, D. Wang, C. Han, Q. An, L. Mai, *ACS Appl. Mater. Interfaces* **2017**, *9*, 17060.
[14] M. M. Huie, D. C. Bock, E. S. Takeuchi, A. C. Marschilok, K. J. Takeuchi, *Coord. Chem. Rev.* **2015**, *287*, 15.
[15] H. Dong, Y. Li, Y. Liang, G. Li, C.-J. Sun, Y. Ren, Y. Lu, Y. Yao, *Chem. Commun.* **2016**, *52*, 8263.
[16] Y. Yan, B, L.i , W. Guo, H. Pang, H. Xue, *J. Power Sources* **2016**, *329*, 148.
[17] S. K. Park, W. M. Dose, B. D. Boruah, M. De Volder, *Adv. Mater. Technol.* **2021**, *7*, 2100799.
[18] T. Luo, Y. Liu, H. Su, R. Xiao, L. Huang, Q. Xiang, Y. Zhou, C. Chen, *Electrochim. Acta* **2018**, *260*, 805.
[19] M. Rashad, M. Asif, I. Ahmed, Z. He, L. Yin, Z. X. Wei, Y. Wang, *J. Magnesium Alloys* **2020**, *8*, 364.
[20] F. Théobald, R. Cabala, J. Bernard, *J. Solid State Chem.* **1976**, *17*, 431.
[21] J. Landesfeind, D. Pritzl, H. A. Gasteiger, *J. Electrochem. Soc.* **2017**, *164*, A1773.
[22] J. Bisquert, G. Garcia-Belmonte, F. Fabregat-Santiago, A. Compte, *Electrochem. Commun.* **1999**, *1*, 429.