HIGHLY EFFICIENT, FLEXIBLE, AND SELF-HEALABLE MOISTURE-DRIVEN ENERGY HARVESTER BASED ON 2D VANADIUM PENTOXIDE NANOSHEETS

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ABSTRACT

Herein we present a flexible and self-healing moisture-induced power generator consisting of Vanadium pentoxide (V_2O_5) nanosheet membrane to harness electricity from ambient moisture. The highly negative surface charge of the V_2O_5 nanosheets directs preferential flow of cations from dissociated water molecules through its nanochannels. The diffusion of these ions from the moisture rich to moisture deficient side of the membrane give rise to a potential gradient and current generation across the membrane. This moisture-triggered device boasts an open circuit voltage of 0.4V and a short circuit current of 0.3μA. Remarkably, any physical damage on V_2O_5 membrane can be effortlessly remedied with the simple addition of a drop of water. Individual devices can be connected in series or parallel to enhance the output power.

KEYWORDS

Blue energy harvest, electrokinetic energy generation, nanofluidics, self-healing membranes

INTRODUCTION

Moist electric nanogenerators (MEGs) systems represent an emerging approach capable of harnessing significant electrical energy from the omnipresent water molecules in the natural environment.[1] Unlike alternative spontaneous energy sources such as mechanical generators, solar cells, and geothermal energy generation, which rely heavily on specific factors like light intensity, water flow, or geothermal heat, MEGs systems exhibit remarkable adaptability to varying environmental conditions. As a result, they have garnered substantial interest among researchers in recent years. Ever since the introduction of moisture power technology in 2015 marked a pivotal moment in this field. Researchers have identified inorganic materials with extensive surface areas, abundant voids, high hydrophilicity, and charged surfaces, such as graphene oxide,[2] porous carbon films,[3] and metal oxides,[4] as prime candidates for achieving exceptional MEGs performance. The origin of this moisture-induced electric power has been explained by a number of mechanisms, including gradient diffusion, streaming potential, and charged surface potential.[5] As the water molecules comes in contact with the charged materials, it undergoes polarization to form charged ionic species. These charged hydrated ions subsequently migrate directionally, moving from regions of high concentration to those with lower concentrations due to the driving force of the concentration gradient. This phenomenon is responsible for the generation of electric energy. Building upon the principles of the Moisture-Enabled Electricity Transfer method, a range of electricity generators have been developed using 2D materials such as, Graphene oxide, Mxene, and so on.[6] These 2D material-based systems exhibit remarkable efficiency in responding to changes in environmental humidity to generate power. Nevertheless, the tightly packed stacking structure, substantial size, and limited active sites of 2D sheets present significant challenges by impeding the adsorption of moisture and the transport of hydrated ions. These obstacles, in turn, significantly hinder the overall performance of power generation.

Herein we report a nanofluidic membrane of reconstructed V_2O_5 Nanosheets to harvest energy from ambient moisture. The V_2O_5 membrane is fabricated by simple restacking of V_2O_5 nanosheets by vacuum filtration.[7] Owing to their outstanding proton conductivity,[8] V_2O_5-based devices displayed high energy density. Moreover, the nanofluidic membrane of V_2O_5 can heal its structural damages by application of water droplet, which further supports its longevity under the practical scenario.

MATERIALS

V_2O_5 synthesis: In the process of synthesizing V_2O_5 nanosheets, V_2O_5 powder was subjected to a treatment involving hydrogen peroxide (H_2O_2) in an ice-cold environment. Typically, 1 gram of V_2O_5 powder was dissolved in 25 mL of deionized water. This was followed by placing the conical flask in an ice bath while maintaining continuous stirring. Gradually, 25 mL of 30% H_2O_2 was added to monitor the formation of an orange-tinted clear solution, accompanied by vigorous oxygen bubbling and the creation of a dark brown precipitate, ultimately yielding a thick, gel-like solution. The as-prepared solution was allowed to stand undisturbed overnight. Subsequently, it was diluted with 150 mL of deionized water and subjected to an hour of ultrasonication in a water bath. This process contributed to the refinement and homogenization of the solution.

Membrane fabrication: The freshly prepared V_2O_5 dispersion is subjected to vacuum filtration, utilizing a polytetrafluoroethylene (PTFE) membrane filter with a pore size of 0.1 micron to obtain a standalone and pliable V_2O_5 membrane once it has been thoroughly dried.

MEG Device fabrication:

The MEG device was fabricated by sandwiching a square piece of V_2O_5 membrane (1 × 1 cm) between a perforated and solid copper electrode using PET as a separator to avoid shorting of the two copper electrodes. The experiments are performed in a humidity-controlled chamber.

RESULTS AND DISCUSSION

The ultra-confined spaces between V_2O_5 nanosheets were created using a vacuum-assisted filtration process, starting with V_2O_5 nanosheets obtained through H_2O_2 exfoliation of bulk V_2O_5 powder, as previously described.[7] Atomic force microscopy (AFM) analysis, as depicted in Figure 1a, reveals that the lateral size distribution of the V_2O_5 nanosheets ranges from 100 nm to 120 nm, with an average thickness of 3-10 nm. The zeta potential analysis of the V_2O_5 dispersion yielded a measurement of -40 mV, which signifies the prevalence of negative surface charges on the V_2O_5 surface. The negative surface charge on the V_2O_5 nanosheets is responsible for the selective cation transport through the channels. To create a well-organized lamellar structure containing percolated network of nanochannels, the nanosheets dispersion was vacuum filtered over a PTFE support membrane to form a free-standing lamellar membrane which separates out of the support membrane on drying. A photo of the as formed lamellar membrane is shown in Figure 1b. For a closer examination of the lamellar structure, the cross-sectional scanning electron microscope (SEM) image displayed in Figure 1c showcases a consistent stacking pattern. This

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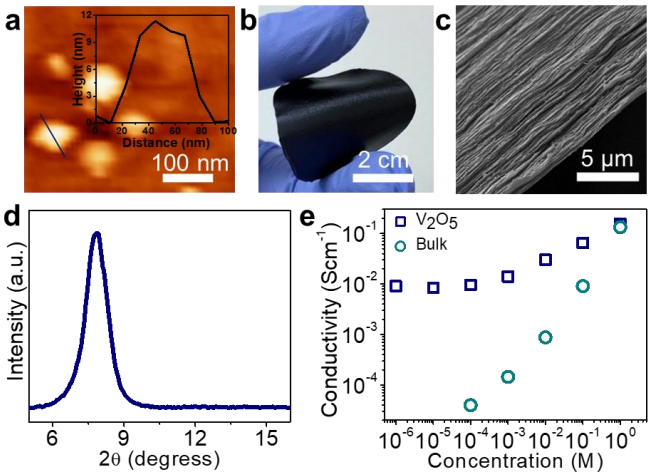

Figure 1: *(a) AFM image of exfoliated V_2O_5 nanosheets. (b) Photo of the restacked membrane of V_2O_5 nanosheets. (c) Cross-sectional SEM image showing lamellar stacking of the V_2O_5 nanosheets. (d) pXRD of the restacked membrane shows interlayer spacing of 1.2 nm. (e) Ionic conductivity as a function of HCl concentration through the restacked V_2O_5 membrane.*

demonstrates the successful formation of the desired structural configuration. Furthermore, the X-ray diffraction (XRD) pattern in Figure 1d exhibits a distinctive and well-defined peak at d = 1.2 nm, which corresponds to the interlayer spacing in the c-direction (001 plane).[9, 10] This peak reflects the highly ordered nature of the nanosheet stacking within the V_2O_5 membrane and confirms the integrity of the desired structural arrangement. The presence of a percolated network of hydrated V_2O_5 channels is further demonstrated by investigating the ion-transport behavior through the two-dimensional nanofluidic channels of V_2O_5. The nanofluidic device composed of V_2O_5 was created by embedding a rectangular V_2O_5 membrane strip (measuring 20 mm × 4 mm × 0.033 mm) within a poly(dimethylsiloxane) (PDMS) elastomer. The ends of the strip were exposed by carving into the PDMS elastomer. These ends were then introduced to an aqueous KCl solution of varying concentrations, while the current vs voltage (I–V) curves of the nanofluidic device were monitored using a Keithley 2450 sourcemeter. The ionic conductivity of the V_2O_5 nanofluidic device, calculated from the slope of the I–V curves, was plotted against electrolyte concentration and compared with bulk electrolyte concentration, as depicted in Figure 1e. While the bulk solution's conductivity varied linearly with concentration, the V_2O_5 membrane-based nanofluidic device displayed two distinct conductivity regimes, characteristic of surface-charge-governed ionic transport behavior.

The negatively charged percolated channels of V_2O_5 membrane is explored to fabricate the V_2O_5-moist electric generator (V_2O_5-MEG) from ubiquitous moisture present in the atmosphere. The schematic representation of V_2O_5-MEG device fabrication is shown in Figure 2. The MEG device was fabricated by sandwiching a square piece of V_2O_5 membrane (1 × 1 cm) between a perforated

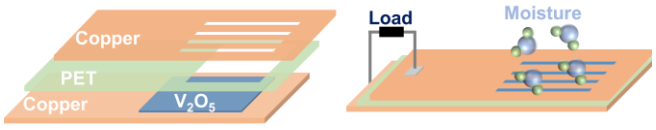

Figure 2: *(a) Schematic of the MEG fabrication.*

and solid copper electrode using PET as a separator to avoid shorting of the two copper electrodes. In a controlled humidity chamber, exposing the V_2O_5-MEG device to 85% relative humidity (RH), manifests an open circuit voltage of 0.42 V and a short-circuit current of 0.3 µA. The results are plotted in Figures 3a and 3b. The generation of potential difference and output current is ascribed to the continuous diffusion of the dissociated water molecules from the perforated copper electrodes to the solid electrode. The mechanism of the process is shown schematically in Figure 3c. Water molecules consist of one oxygen atom and two hydrogen atoms, creating a

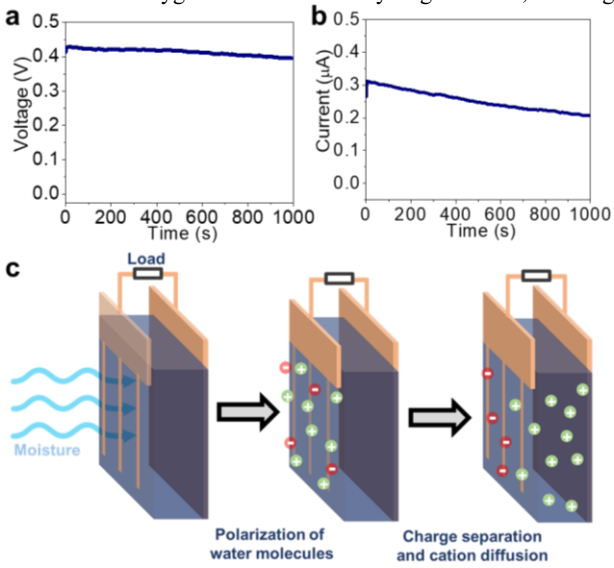

Figure 3: *(a) Open circuit voltage and (b) short-circuit current fat 85% relative humidity for 1000 seconds. (c) Mechanism of power generation by the V_2O_5-MEG.*

polarized structure due to electron transfer.[11] This polarization fosters hydrogen bonds, allowing water molecules to attract each other, resulting in dynamic bond breaking and making.[12] This dynamic process enables proton transfer between molecules. Consequently, water hosts trace amounts of ions like H_3O^+ and OH^-. So also, recent research suggests the presence of H_2O^+ and H_2O^- ions formed by electron delocalization.[13] Now, owing to the negative surface charge of the V_2O_5 nanosheets ultrafine height of the V_2O_5 nanochannels (~1.3 nm) which is significantly smaller than the Debye length of deionized water (961 nm),[14] the electrical double layer (EDL) of opposite walls of V_2O_5 channel overlaps and selectively allows diffusion of positive ion of the dissociated water. This uni-directional flow of ions is balanced by the flow of electrons externally through the circuit, essentially generating power. By connecting the two sides of the membrane to copper (Cu) electrodes, an interface for electron transfer is established.

To assess the influence of device performance on moisture absorption, the device was subjected to diverse humidity conditions. The observed output potential exhibits a positive correlation with escalating humidity levels, as depicted in Figure 4. The augmentation in humidity engenders a greater influx of protons to one side of the channels, thereby amplifying the electrochemical gradient. This heightened gradient, in turn, results in an increased potential disparity between the two electrodes. One notable feature of the V_2O_5- MEG device is its ability to self-repair physical damage to the active material simply by adding a drop of water. To demonstrate this healing capability, two rectangular strips of V_2O_5 membrane (20 mm × 10 mm × 0.033 mm) were brought into contact,

and a 10 µL water droplet was applied to the junction. Once the water evaporated, the two strips seamlessly fused into a single strip, with the healed membrane exhibiting the same flexibility and

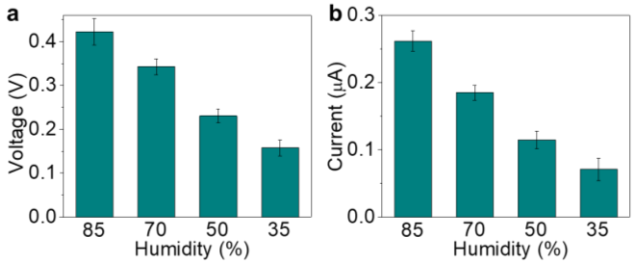

Figure 4: *(a) Open circuit voltage and (b) short-circuit current demonstrated by the V_2O_5- MEG at different humidity levels. (d) Open circuit voltage and short-circuit current as a function of membrane thickness.*

strength as the original one. To validate this healing process further, the mended strip was subjected to tension until it ruptured. Interestingly, the healed membrane fractured at a location distinct from the healed region, as depicted in Figure 5a. The augmented mechanical strength of the healed membrane was attributed to the increased thickness in the healed area. In freestanding membranes, the bonding of individual sheets involves cross-linking of nanosheets by trace cations (V^{2+}, V^{3+}, and VO^{2+}) released during the exfoliation process, along with inter-sheet attractions like van der Waals forces and hydrogen bonding.[15] In the presence of liquid water, these interactions extend between strip surfaces, leading to strip fusion. Upon water evaporation, the interactions within and between V_2O_5 flakes remain consistent. Importantly, the energy generation properties of the membrane fully recover through the healing process, as evident in Figure 5b and 5c, where both healed and pristine V_2O_5 strips (20 mm × 10 mm × 0.033 mm) exhibit comparable current and voltage values, affirming the effective restoration of the V_2O_5 membrane. Individual MEGs can be

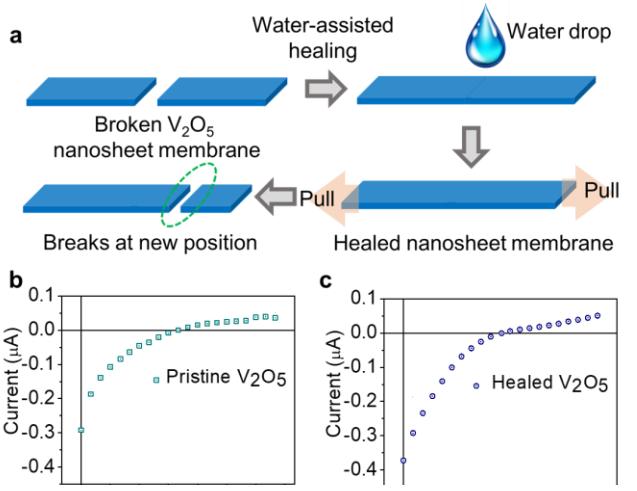

Figure 5*: (a) Schematic showing the water-assisted healing of the V_2O_5 nanosheet membrane. IV curves showing open circuit voltage and short-circuit current for the (a) Pristine and (b) healed membrane.*

connected in series and parallel to enhance the voltage and current output. Figure 6a shows voltage output for eight MEGs connected in series at 85 % RH. We also demonstrate the concept of artificial tree, where the V_2O_5-MEG are connected in various series/parallel configuration to enhance power output. These types of MEGs can be used in remote areas to power streetlights and other small sensors as illustrated in Figure 6b.

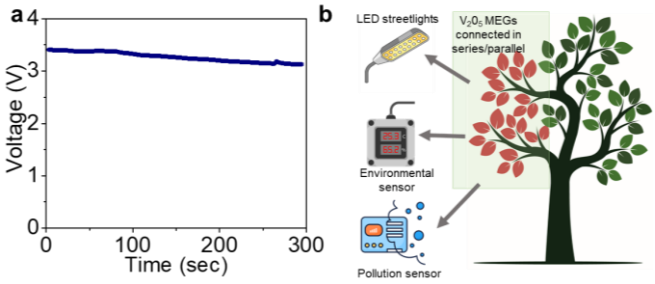

Figure 6: *(a) Open circuit voltage demonstrated by eight MEGs connected in series. (b) Schematic showing possible application of the MEG devices to power up small electronics.*

CONCLUSION

A pliable and self-healable Moisture Electric Generator was constructed employing two-dimensional nanosheets of Vanadium Pentoxide (V_2O_5). Under conditions of 85% relative humidity, the device demonstrates an open circuit voltage of 0.42 V and a short-circuit current of up to 0.3 µA. The generated output potential exhibits sensitivity to both moisture levels and the thickness of the utilized membrane. Notably, a physically damaged V_2O_5 membrane can be swiftly restored by applying a droplet of water to the damaged site, highlighting the self-healing capability. For scalability, individual devices can be interconnected in series and parallel configurations, facilitating the powering of small-scale electronic devices.

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