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The impact of processing voltage of wire electric discharge machining on the performance of Mo doped V–VO_{0.2} based Archimedean micro-supercapacitors†

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Vanadium oxide-based electrode materials have attracted increasing attention owing to their extraordinary capacitance and prolonged lifespan, excellent conductivity and outstanding electrochemical reversibility. However, the development of vanadium oxide-based integrated electrodes with outstanding capacitive performance is an enduring challenge. This research reports a facile method for structuring 3D Archimedean micro-supercapacitors (AMSCs) composed of Mo doped V–VO_{0.2} (Mo@V–VO_{0.2}) based integrated electrodes with designable geometric shape, using computer-aided wire electric discharge machining (WEDM). The performance of Mo@V–VO_{0.2} based AMSCs manufactured by different processing voltages of 60 V, 80 V and 100 V were evaluated. It was found that 80 V is the optimal processing voltage for manufacturing Mo@V–VO_{0.2} based AMSCs with the best electrochemical performance. This device demonstrates superior capacitive behavior even at an ultra-high scan rate of 50,000 mV s⁻¹, and achieves a good capacitance retention rate of 94.4% after 2000 cycles. Additionally, the characteristics of electric field distribution were also simulated for optimizing the geometric structure of the microdevices. This WEDM fabrication technique, which is easy, secure, patternable, efficient, economical, eco-friendly, and does not require binders or conductive additives, enables the development of high-capacity 3D pseudocapacitive micro-supercapacitors and demonstrates the great potential for metal oxide synthesis and microdevice manufacturing.

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1. Introduction

With the prevalent utilization of microscale electronic devices, miniaturization and integration technologies have become a critical focus.¹ Currently, significant advancements have been achieved in microscale electronic devices such as portable, wearable sensors and flexible displays, but the development of energy storage devices has lagged behind other electronic

devices. Furthermore, a compelling demand exists for downsizing energy storage devices in sectors like healthcare and aviation.² Consequently, the spotlight has turned to micro-supercapacitors (MSCs) and micro-batteries with small sizes, easy integration, and high energy storage capacity.^{3,4} However, the present micro-batteries are hindered by their slow charging rates and short operational lifespan, which leads to frequent replacements after hundreds to thousands of recharging cycles.^{5,6} In contrast to micro-batteries, MSCs exhibit an extended lifecycle, capable of enduring thousands or more charge–discharge cycles, which can effectively reduce the frequency of replacements.⁷ Furthermore, MSCs have exceedingly rapid charge and discharge rates, which enable them to efficiently accumulate and discharge significant electrical energy in a short time. Moreover, MSCs are environmentally friendly due to their extended lifespan and infrequent replacement requirements.^{8–10} Additionally, the membrane-free structure design of MSCs facilitates high-efficiency ion diffusion and effectively prevents the occurrence of a short-circuit.¹¹ Therefore, due to the above advantages, MSCs have received a lot of attention and are popular in terms of energy storage. Carbon

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based MSCs attract researchers' attention because of their fast charging/discharging rate, long cycling life and good flexibility.¹² In contrast to carbon based MSCs, pseudocapacitive micro-supercapacitors (PC-MSCs) demonstrate a substantially higher specific capacitance. This is because the capacitance of the carbon based MSCs is derived from the accumulation of charge at the electrode/electrolyte interface, while PC-MSCs achieve a superior electrical capacity through the rapid and reversible redox reaction occurring at the electrode.¹³

At present, a variety of fabrication methods, including conventional photolithography,^{14,15} screen printing,¹⁶ inkjet printing,¹⁷ 3D printing,¹⁸ stamping,¹⁹ laser direct writing,²⁰ plasma etching,²¹ and mask-assisted filtering,²² have been developed for the production of planar MSCs. Unfortunately, the current manufacturing methods have suffered from obvious constraints in manufacturing of MSCs. For instance, the template or photoresist utilizing in traditional photolithography must be removed using a buffer solution and extreme high temperature exposure is also involved in the device processing procedures.²³ These will lead to a decrease in the fabricated efficiency and the performance of MSCs.²⁴ Screen printing often results in uneven ink coating on the substrate, which greatly affects the capacitive behavior of the whole device. In addition, the preparation of the patterning silk screen will inevitably raise production expenses, especially in large-scale production.^{16,25} Moreover, since 3D printing is a process of layer-by-layer construction, the surface of the manufactured capacitor may have roughness, burrs or other surface defects, which may affect the performance and stability of the capacitor. Furthermore, the limited materials currently available for 3D printing inks restrict the further development of MSCs with customized capacitive performance.²⁶ Moreover, low conducting binders was normally used for ink processing, which inevitably results in poor conductivity of the devices, especially at high charging/discharging rates. Recently, laser manufacturing technique has been developed for manufacturing MSCs, but it necessitates costly machinery with precision management and accurate operational control, which requires high standards from the manufacturing process. Additionally, laser manufacturing may result in material localized heating, which can cause thermal stress problems and impact the effectiveness and stability of the MSCs. Furthermore, conventional laser-processed materials, such as carbon-based materials and graphene, often result in low capacitance for MSCs.²⁷⁻²⁹ Aim to enhance the capacitance, various laser processing techniques have been explored to manufacture different PC-MSCs. For instance, Liu *et al.*³⁰ investigated a flexible in-plane hybrid MSCs based on Fe₃O₄ nanoparticles anchored porous laser-induced graphene. This investigation proved that Fe₃O₄ based PC-MSCs showed more than 100 times higher specific capacitance than that of graphene based MSCs.

There has been a growing interest in the fabrication of high performance PC-MSCs with various active materials, encompassing polypyrrole (PPy),³¹⁻³³ polyaniline (PANI),³⁴ poly(3,4-ethylenedioxythiophene) (PEDOT),³⁵ FeOOH,³⁶ Cu(OH)₂,³⁷ Fe₃O₄,³⁸ Mn₃O₄,³⁹ NiFe₂O₄,⁴⁰ RuO₂,⁴¹ NiCo₂S₄,⁴² MoS₂,⁴³ and MXene.^{44,45} Transition metal oxides are often utilized as

electrode materials for supercapacitors because of their higher specific capacitance and better cyclic stability compared to most conductive polymers.⁴⁶ Vanadium oxides distinguish themselves from most transition metal oxides by offering access to four readily interconvertible valence states (II–V). Vanadium oxides based materials are recognized as advanced active materials for strong power electrochemical capacitors owing to their extraordinary capacitance and prolonged lifespan, excellent conductivity and outstanding electrochemical reversibility.^{47,48} For example, Zhang *et al.*⁴⁹ developed a simple laser ablation method for preparing VO_x/reduced graphene oxide (rGO) composites with hierarchical structures. Minyawi *et al.*⁵⁰ fabricated a stable ink for screen printing, using a non-poisonous solvent and vanadium dioxide (VO₂). The performance was further improved by hybridization with gold nanoparticles. Zhou *et al.*⁵¹ fabricated V₂O₅ based MSCs with ordered porous layered structure and uniform electric field intensity by combining various strategies, such as micro-ultrasonic, vacuum filtration and 3D printing technology. Moreover, Zhou *et al.*⁵² prepared a high-performance composite 3D printing inks by adopting NiCo-metal-organic frameworks (MOFs) @CoOOH@V₂O₅ as active materials, and using carbon nanotubes and graphene oxide for adjusting their electronic conductivity and rheology behavior. Although researchers achieved enhanced capacitive performance of vanadium oxide based electrode materials and devices, the aforementioned complex processes for manufacturing PC-MSCs require costly materials, extra conductive media, toxic chemicals, and extra current collectors, inevitably resulting in high manufacturing expenses and low production efficiency.⁵³ Furthermore, their areal capacitances are still significantly below the required levels for commercial application. Recently, an increasing research interest have been focused on the development of 3D conductive network, such as 3D carbon network and 3D MXene-MOFs, for tailoring the physical or chemical properties of various composite materials.⁵⁴⁻⁵⁶ In order to boost their areal capacitances, researchers have developed a variety of 3D current collectors for PC-MSCs, which play a crucial role in enhancing electron transfer and facilitating the fast diffusion of electrolyte ions.^{37,57} For instance, Liu *et al.*⁴⁵ grew MXene on 3D MOFs to prepare 3D MXene-MOFs composites to boost the electrochemical performance of supercapacitors. It was found that 3D MOFs could effectively prevented the aggregation of MXene, which is beneficial for promoting electrolyte access and improving conductivity. Xie *et al.*⁵⁸ adopted laser engraving to fabricate 3D interdigitated Ni foams current collectors for electrodeposition of MnO₂ and PPy pseudocapacitive materials for PC-MSCs. Jiang *et al.*⁵⁹ fabricated 3D Nickel foam interdigitated current collectors using laser machining. Subsequently, NiCo₂S₄ based interdigitated positive electrode and carbon nanofiber based interdigitated negative electrode were prepared by hydrothermal synthesis and chemical vapor deposition strategy, respectively for constructing NiCo₂S₄/carbon nanofiber hybrid devices. Their results indicated that the areal capacitance, cyclic stability and rate performance of the fabricated PC-MSCs have been improved remarkably. This is because 3D electrode configuration design offers many merits, including



preparation of electrode materials with good electronic conductivity, high surface area, good structural stability and shortened electron/ion diffusion length, which facilitated fast ion and electron transport. However, the processes involved in fabricating 3D PC-MSCs are multifaceted and require numerous complex procedures, resulting in an unavoidable increase in production cost. Therefore, there is an urgent need for manufacturing high electrochemical performance 3D PC-MSCs with a simple, environmental-friendly and efficient technology, which is free from binders, surfactants, conductive additives, and templates.

Wire electrical discharge machining (WEDM) is a non-traditional machining technique using spark erosion effect to fabricate workpiece with various hardness and complex 3D structures for various applications, such as aerospace, automobiles, atomic reactors and PC-MSCs.^{60–63} WEDM could fabricate PC-MSCs electrodes with complex geometries at one step without using any aids of chemicals, surfactants, binders, gases, conductive additives, additional current collectors and templates. Moreover, this single step WEDM manufacturing strategy greatly simplifies the fabricated procedures of micro-electrodes as it does not require the assistance of additional processes, such as annealing, dispersing, filtering, vacuuming, gas-supplying, centrifugation and ultrasonication. It has been reported that the processing voltage of WEDM showed great influence on the surface morphologies of the machining substrates.⁶⁴ However, up to now, there is a lack of research investigating on the effect of WEDM processing voltage on the electrochemical performance of PC-MSCs. Therefore, this investigation aims to elucidate the relationship between machining voltages and the electrochemical properties of PC-MSCs fabricated by the specific technique of WEDM. In this context, we developed a single step WEDM to fabricate 3D Mo@V-VO_{0.2} based PC-MSCs with customized patterns. During WEDM processing, computer-aided manufacturing is utilized to shape a vanadium metal plate into a 3D current collector with Archimedean patterns. At the same time, the elevated temperatures generated within the discharge channels trigger oxidation and Mo doping on the surface of these 3D vanadium current collectors to form 3D Mo@V-VO_{0.2} integrated electrodes and devices. Another important finding is that the performance of the 3D Mo@V-VO_{0.2} based PC-MSCs could be tailored by the processing voltage of WEDM. It was found that 80 V is the optimal processing voltage for manufacturing Archimedean micro-supercapacitors (AMSCs) with the best electrochemical performance. This device demonstrates superior capacitance even at an ultra-high scan rate of 50,000 mV s⁻¹, and maintains a good capacitance retention rate of 94.4% after 2000 cycles. It is important to note that these devices were manufactured without the expensive machinery, manufacturing conditions, toxic or costly materials, or convoluted fabrication processes. Consequently, the production of these 3D Mo@V-VO_{0.2} based PC-MSCs can be streamlined into a straightforward one-step process, eliminating the need for low conductive binders, surface modified agents, extra current collectors and high conductivity additives.

2. Experimental procedures

2.1 Materials

Vanadium metal sheet (V-MS) was supported by the company of Qinghelisheng Metal Materials. The high efficiency WEDM Mo wire was supported by Jinduicheng Molybdenum Mining Guangming Corporation. The KOH solutions were supported by Kell Chemical Technology Company.

2.2 Preparation of Mo@V-VO_{0.2} based electrodes and PC-MSCs

Mo@V-VO_{0.2} based integrated electrodes were prepared using V-MS as starting material by computer-controlled WEDM method, and then the integrated electrodes were cut into 3D Mo@V-VO_{0.2} based integrated devices using the same technology. The device was fabricated in deionized water and processed at three different processing voltages of 60 V, 80 V and 100 V, respectively.

2.3 Materials and electrochemical characterization

TESCAN MIRA LMS scanning electron microscope (SEM) was adopted to analyze the surface morphology. For electrode material characterization, X-ray photoelectron spectroscopy (XPS) testing was performed by a thermal science K-Alpha instrument. The V-VO_{0.2} integrated electrode was subjected to X-ray diffraction (XRD) analysis using a Rigaku K α K α diffractometer at a scan rate of 2° min⁻¹. Transmission Electron Microscope (TEM) was performed using Thermo Fisher Helio Nanolab G3 UC instrument. Energy Dispersive X-Ray Spectroscopy (EDX) was performed with Thermo Fisher Talos F200s equipment to analyze the element distribution of electrode material. The oxygen vacancies of electrode material was investigated by Electron Paramagnetic Resonance (EPR) using Bruker EMXplus-6/1 instrument. Cyclic voltammetry (CV) and galvanostatic charge-discharge (GCD) studies were performed using a CHI 660E electrochemical workstation. The CV experiments were studied at scanning rates ranging from 1 to 50 000 mV s⁻¹, within a potential window of 0–0.6 V. The GCD examination was conducted within a current density range of 0.2–2 mA cm⁻² at a testing potential range of 0–0.6 V. The capacitive properties of single PC-MSCs in KOH electrolyte with a concentration of 1 M were analyzed by CV and GCD. The testing area of all the devices is equal to 1 cm².

3. Results and discussion

Fig. 1 shows the efficient fabricating process of Mo@V-VO_{0.2} based integrative PC-MSCs using WEDM technique. The Mo doped VO_{0.2} active material grown from V-MS and Mo cutting wire is used for energy storage. Fig. 1a shows the untreated V-MS under the support of the jig and fixture. Subsequently, the surface of the V-MS was synchronously oxidized and doped with Mo by the treatment of WEDM (Fig. 1b). Fig. 1c shows the locally amplified WEDM discharge channel diagram between the V-MS and Mo cutting wire experiencing high temperature oxidation and element doping to form Mo doped VO_{0.2} active



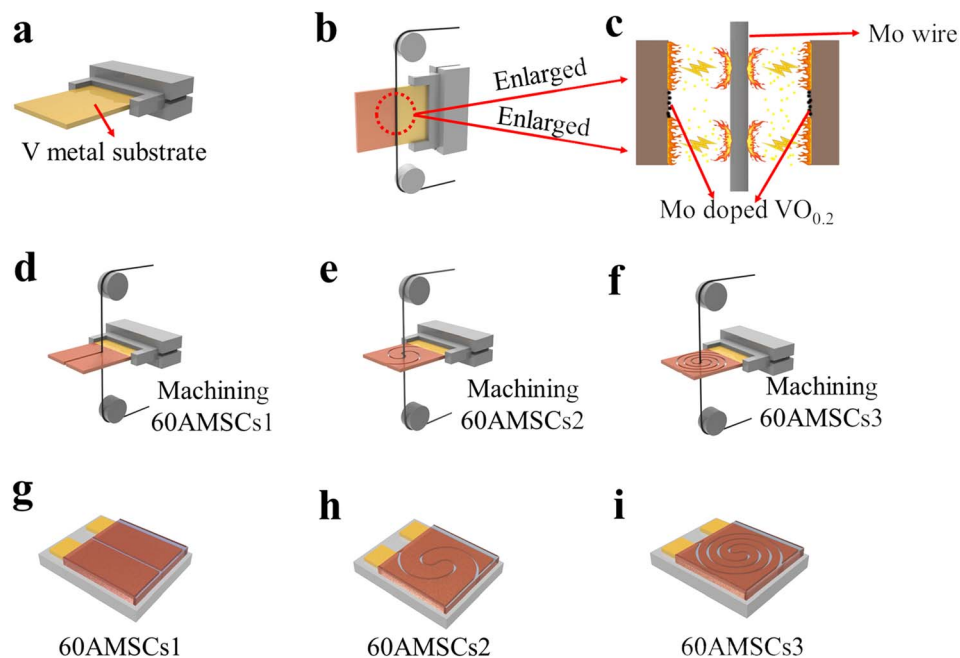


Fig. 1 (a) Untreated V-MS and (b) V-MS during WEDM and (c) enlarged electric discharge channel for generating Mo doped $\text{VO}_{0.2}$ particles during WEDM and (d–i) manufacturing process of Mo doped $\text{VO}_{0.2}$ PC-MSCs devices with different modes.

material. Thereby, the treated $\text{Mo@V-VO}_{0.2}$ based integrated electrode is cut directly into a $\text{Mo@V-VO}_{0.2}$ based PC-MSCs device with a specified 3D pattern *via* WEDM with computer-aided control system (Fig. 1d–f). The microdevices with one-trip Archimedean shape (60AMSCs1), two-trips Archimedean shape (60AMSCs2) and three-trips Archimedean shape (60AMSCs3) were prepared by one-step WEDM technique, respectively (Fig. 1g–i). It's important to highlight that WEDM, which benefits from a computer-aided manufacturing process, offers the merits of simplicity, safety, and cost-effectiveness. Moreover, according to the pre-set processing program of the computer, the surface morphology of $\text{Mo@V-VO}_{0.2}$ based integrated electrodes and geometric shape of the microdevices could also be controlled automatically. Moreover, the whole manufacturing process eliminates the usage of dangerous chemicals and toxic solvents, which is very beneficial for environment protection.

Morphological characteristics of the $\text{Mo@V-VO}_{0.2}$ electrodes were examined using SEM characterization. The surface morphology of V-MS before processing by WEDM is smooth without any microstructure features (Fig. 2a). Fig. 2b–d shows the images of $\text{Mo@V-VO}_{0.2}$ integrated electrodes treated at different applied voltages of WEDM. At a processing voltage of 60 V, the $\text{Mo@VO}_{0.2}$ particles are sparse, whereas at 100 V they grow larger and show severe agglomeration. Compared to 60 V and 100 V, the surface morphology of the $\text{Mo@VO}_{0.2}$ particles fabricated at 80 V is relatively dense and uniform, which is beneficial for energy storage. Fig. 3a shows the XRD patterns of V-MS without WEDM treatment and with the WEDM cutting treatment carried out at processing voltages of 60, 80 and 100 V, respectively. The XRD pattern of raw V-MS revealed diffraction peaks located at 42.1° , 61.2° and 76.8° , which can be indexed

to V, corresponding to the (110), (200) and (211) crystal planes, respectively.⁶⁵ The XRD patterns of V-MS treated by processing voltages of 60, 80 and 100 V showed similar broad diffraction peaks corresponding to the PDF #10-0321. These diffraction peaks positioned at 40.1° , 43.0° , 62.4° and 76.8° correspond to $\text{VO}_{0.2}$ indexing to the crystal planes of (101), (110), (200) and (211), respectively. But the material also contained amorphous phase, indicating relatively low crystallized of $\text{VO}_{0.2}$ was obtained. This phenomenon was also confirmed by the selected area electron diffraction (SAED) pattern achieved by TEM examination (Fig. 1S[†]). Fig. 3b displays the high-resolution V 2p spectrum obtained from XPS analysis of a $\text{Mo@V-VO}_{0.2}$ electrode prepared by the WEDM. The XPS spectra were calibrated using C

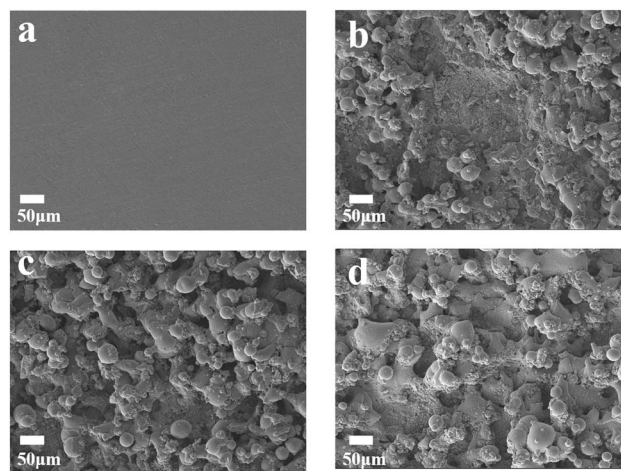


Fig. 2 SEM images of V-MS (a) before vanadium plate processing and integrated electrode at different processing voltages (b) 60 V; (c) 80 V; (d) 100 V.



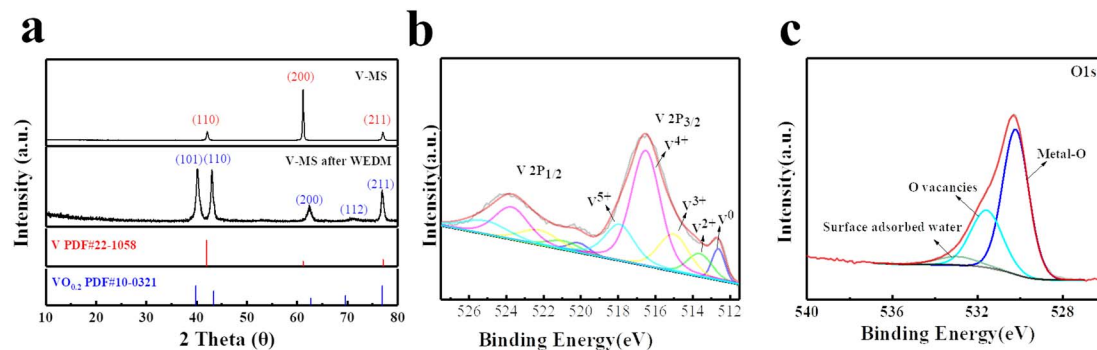


Fig. 3 (a) XRD profiles, and XPS spectra of (b) V 2p and (c) O 1s, for V-MS after WEDM.

1s at 284.8 eV as the reference peak. The peaks observed at 512.6 and 513.6 eV can be attributed to metallic vanadium and V^{2+} oxidation state, respectively.⁶⁶ Moreover, the broad V 2p_{3/2} standard peak at 515.0, 516.5, and 517.9 eV is deconvoluted into three distinct peaks, corresponding to the binding energy of V 2p_{3/2} electrons in the V^{3+} , V^{4+} , and V^{5+} oxidation states, respectively.⁶⁷ Moreover, the energy-dispersive X-ray spectroscopy (EDS) element mapping operated with SEM proved that the elements of Mo, V and O are uniformly distributed on the surface of Mo@V-VO_{0.2} (Fig. 2S[†]). This uniform element distribution phenomenon was also confirmed by EDX carried out with TEM testing (Fig. 1S[†]). The multiple valence state of vanadium oxide with Mo doping facilitates fast electronic transportation, which could greatly boost their electrochemical performance. Fig. 3c shows the O 1s spectrum, which can be deconvoluted into three standard peaks positioned at 530.2, 531.6, and 532.9 eV, which correspond to metal–O bond, O vacancies, and surface adsorbed water, respectively.^{68–70} The generated oxygen vacancies were also proved by EPR testing (Fig. 3S[†]). The sample of 80AMSCs3 showed a *g*-value of 2.0058, closing to that of a free electron (2.0023), which indicated the appearance of unpaired electrons.^{71,72} The introduction of oxygen vacancies in VO_{0.2} is beneficial for accelerating its electronic transportation speed and enhancing its electrochemical performance.

CV tests were performed on 3D PC-MSCs devices with different patterns (60AMSCs1, 60AMSCs2 and 60AMSCs3) fabricated by the same processing voltage of 60 V. Fig. 4a–c show the CV profiles of 60AMSCs1, 60AMSCs2, and 60AMSCs3 devices, respectively. All the obtained CV curves display nearly rectangle shapes, indicating excellent capacitive performance of PC-MSCs devices fabricated *via* WEDM. The areal capacitances of 60AMSCs1, 60AMSCs2, and 60AMSCs3, derived from their respective CV profiles, are illustrated in Fig. 4d. It demonstrates that 60AMSCs3 obtains a higher capacitance of 16.8 mF cm⁻² (1 mV s⁻¹) than that of 60AMSCs1 and 60AMSCs2. The same occurrence was noted at other scanning rates for 60AMSCs1, 60AMSCs2, and 60AMSCs3. This is mainly attributed to the reduction of electrode width which is beneficial for accelerating the ion transport rate. This phenomenon is further proved by the simulations of the electric potential distribution and electric field intensity distribution for 60AMSCs1, 60AMSCs2, and 60AMSCs3 respectively (Fig. 4S[†]).

To explore the capacitive behavior of 60AMSCs1, 60AMSCs2, and 60AMSCs3 devices at ultra-high scan rates, CV testings were conducted from 10 to 50 V s⁻¹ (Fig. 5a–c). The shapes of the CV curve sustained as nearly rectangle, which confirmed the excellent capacitive performance of 3D PC-MSCs devices fabricated through WEDM. This excellent electrochemical performance is due to the 3D binder-free integrated electrode design, Mo doping and multivalent states of vanadium oxide, which enhanced the electrical conductivity of the electrodes and fastened the ion and electron transport. In Fig. 5d, the areal capacitances of devices 60AMSCs1, 60AMSCs2, and 60AMSCs3 are presented, calculated based on their respective CV profiles. Compared to 60AMSCs1 and 60AMSCs2, 60AMSCs3 achieved larger capacitance at the same scan rate, which was consistent with those acquired at 1–100 mV s⁻¹ (Fig. 4), benefiting from the shortened average ions diffusion distance between adjacent electrodes by the reduction of electrode width. Even at 50 V s⁻¹, the areal capacitance of 60AMSCs3 remained at 2.7 mF cm⁻². This is a benefit from the 3D binder-free integrated electrode design, Mo doping, introduction of oxygen vacancies and multivalent states of vanadium oxide, which enhanced the electronic conductivity of vanadium oxide active material and promoted the ion and electron transport efficiency. Fig. 6a displays the GCD profiles of 60AMSCs1, 60AMSCs2, and 60AMSCs3 devices at 0.9 mA cm⁻². The symmetrical triangles of all GCD profiles indicate that good capacitive properties were achieved. Compared to 60AMSCs1 and 60AMSCs2, 60AMSCs3 obtained higher capacitance, which is consistent with the CV examination results shown in Fig. 4 and 5. As shown in Fig. 6b, the areal capacitance values of 60AMSCs3 devices decreased slightly with the increase of the testing current densities from 0.3 to 2 mA cm⁻² and obtained a good capacity retention of 82.5%.

In order to further demonstrate the advantages of WEDM technology in manufacturing 3D Mo@V-VO_{0.2} integrated electrode with controllable surface morphology, the Mo@V-VO_{0.2} based AMSCs3 were manufactured with different WEDM processing voltages (60 V, 70 V, 80 V, 90 V and 100 V), which were named as 60AMSCs3, 70AMSCs3, 80AMSCs3, 90AMSCs3 and 100AMSCs3 respectively. Fig. 7a–c shows the CV curves of 60AMSCs3, 80AMSCs3, and 100AMSCs3 devices at low scan rates from 1 to 100 mV s⁻¹. The box shape CV profiles indicate that Mo@V-VO_{0.2} based PC-MSCs fabricated *via* WEDM have



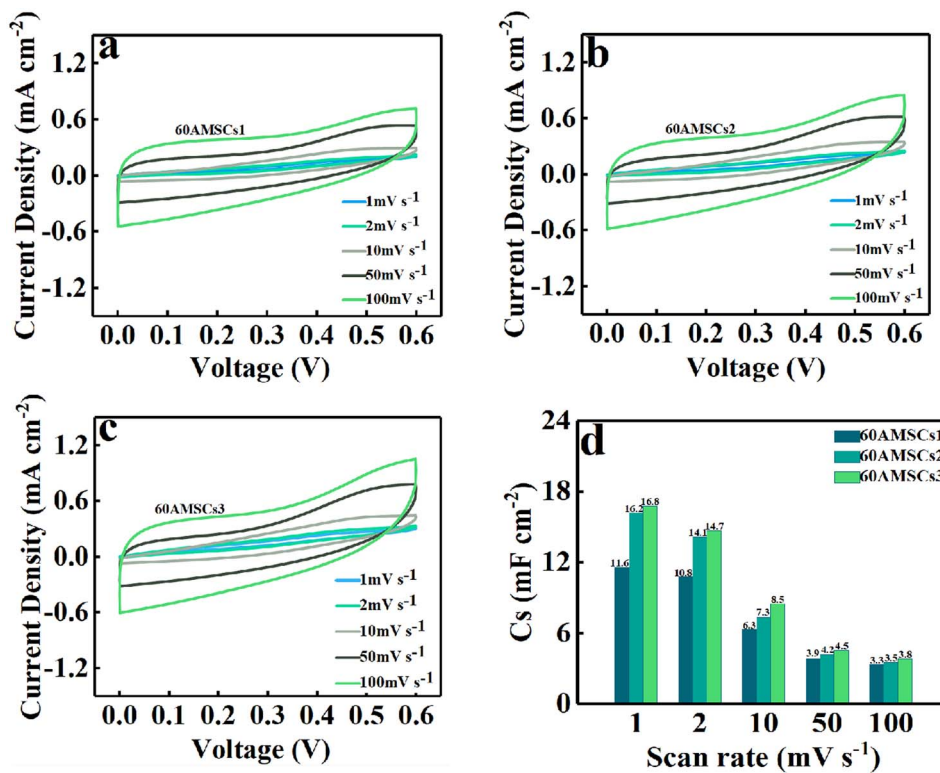


Fig. 4 CVs for (a) 60AMSCs1, (b) 60AMSCs2, (c) 60AMSCs3 at 1–100 mV s⁻¹ and (d) corresponding capacitance derived from CV profiles.

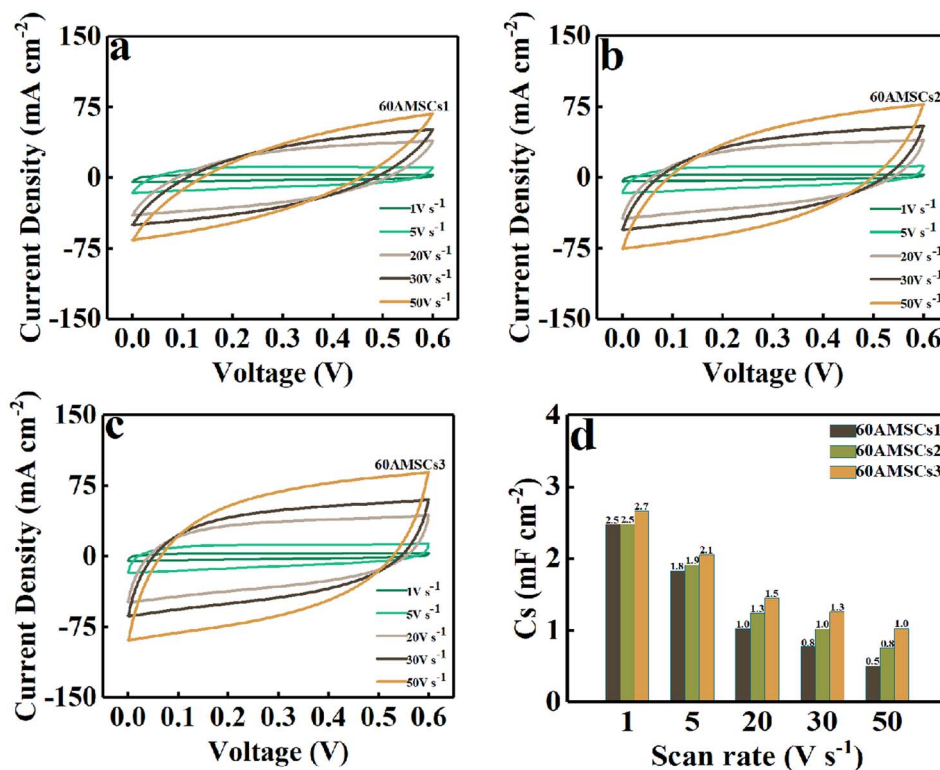


Fig. 5 CVs for (a) 60AMSCs1, (b) 60AMSCs2, (c) 60AMSCs3 at 1–50 V s⁻¹ and (d) corresponding capacitance derived from CV profiles.



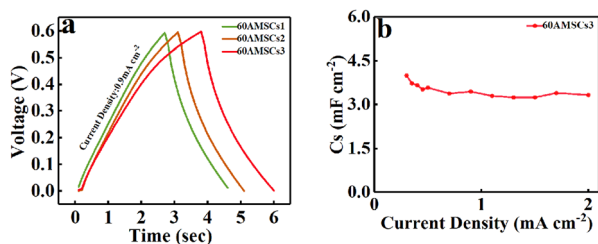


Fig. 6 (a) The GCD images of 60AMSCs1, 60AMSCs2 and 60AMSCs3, (b) corresponding capacitance derived from GCD profiles for 60AMSCs3.

excellent capacitive properties. Fig. 7d showed the areal capacitance of 60AMSCs3, 80AMSCs3, and 100AMSCs3 derived from CV. It is evident that the 80AMSCs3 device achieved the highest capacitance value of 25.2 mF cm^{-2} (at 1 mV s^{-1}) among these three microdevices. The 80AMSCs3 prepared by processing voltage of 80 V also showed the best capacity among these three devices at other different scan rates. This is because the $\text{Mo@VO}_{0.2}$ particles prepared by the processing voltage of 80 V are dense and uniform, providing more active sites for energy storage and thus enhance its electrochemical performance. Moreover, the obtained capacity of 80AMSCs3 is higher than that of 70AMSCs3, 90AMSCs3 (Fig. 5S†), PANI/ V_2O_5 based PC-MSCs fabricated by combined processes of electrodeposition, spray coating, solvothermal method, centrifugation, pyrolysis, annealing and dispersing,⁷³ rGO/ V_2O_5 based PC-MSCs fabricated by compound procedures of spray coating, sputtering, modified Hummer's method, annealing, stirring, filtering and

ultrasonication,⁷⁴ Graphene-PEDOT-poly(styrene sulfonic acid) (PSS) based PC-MSCs fabricated by complex processes of mask-assisted spray deposition, electrochemically exfoliating, stirring, heating and sonication,⁷⁵ MXene based MSCs prepared by combined processes of laser machining, spray coating, etching, stirring, filtering and centrifugation,⁷⁶ carbon nanotubes (CNT) based MSCs manufactured with a combination processes of spin coating, photolithography, ultrasonication, stirring, centrifugation, drying, pyrolysis and baking,⁷⁷ activated carbon prepared by combined processes of inkjet printing, photolithography, chemical vapour deposition, evaporation and etching,⁷⁸ carbon onions based MSCs fabricated by complex processes of electrophoretic deposition, photolithography, etching, thermal growing, annealing and heating,⁷⁹ graphene based MSCs fabricated by complex processes of spin coating, lithography, O_2 plasma treatment, and CH_4 plasma treatment,⁸⁰ graphene based MSCs fabricated by complex processes of laser-scribing, modified Hummer's method, stirring, and drop-cast,⁸¹ and rGO based MSCs prepared by complex processes of laser radiation, vacuum filtration, modified Hummer's method, stirring, filtering, washing and heating.⁸² It has been observed that these existed techniques for fabricating MSCs typically require assistance from other processes, leading to increased complexity in the fabrication procedures. Moreover, the reported techniques normally require the usage of chemicals, surfactants, binders, gases, conductive additives, additional current collectors or templates, which furtherly make the fabricated processes complicated. In contrast, the single step WEDM manufacturing strategy developed in this research not only fabricated MSCs with better capacitive performance but

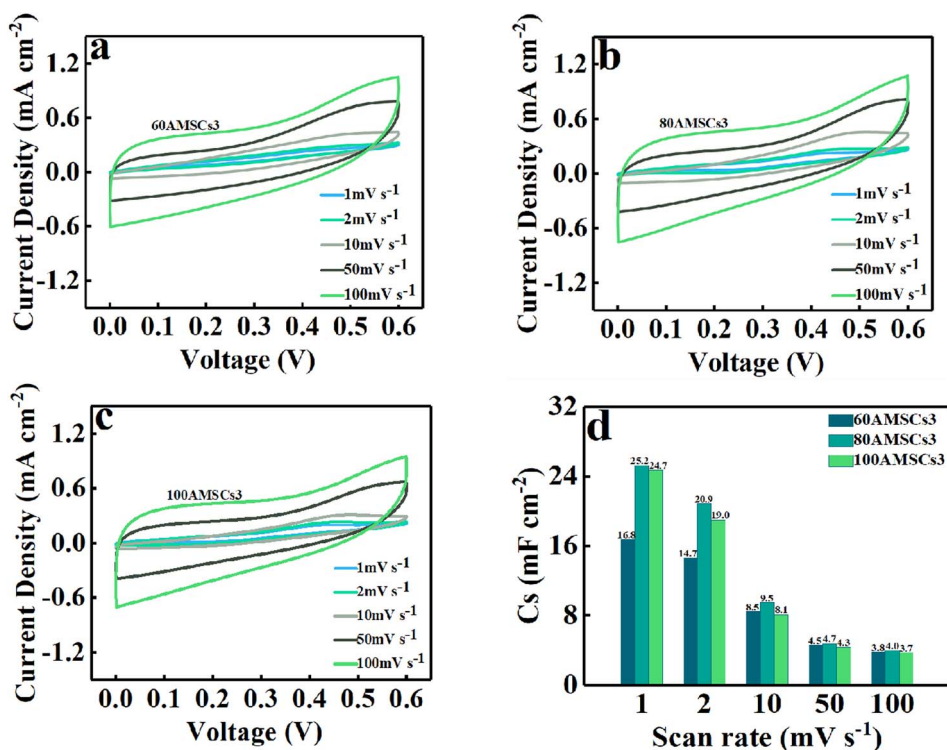


Fig. 7 CVs for (a) 60AMSCs3, (b) 80AMSCs3, (c) 100AMSCs3 at 1–100 mV s^{-1} and (d) corresponding capacitance derived from CV profiles.



also greatly simplified the fabricated procedures of microelectrodes as it does not require the assistance of other manufacturing processes, chemicals, surfactants, binders, gases, conductive additives, additional current collectors and templates. The comparison details about these fabrication techniques for various MSCs were presented at Table 1S.†

To further investigate the capacitive behavior of these devices at ultra-fast charging/discharging rates, CV tests were conducted ranging from 10 to 50 V s^{-1} . The examination results of 60AMSCs3, 80AMSCs3, and 100AMSCs3 are depicted in Fig. 8a–c, respectively. All these CV curves present a quasi-rectangle shape up to 50 V s^{-1} , which is ≥ 50 times higher than that of rGO/ V_2O_5 based PC-MSCs manufactured by combination of chemical synthesis, ultrasonication and spray deposition,⁷⁴ rGO/ VO_x based PC-MSCs manufactured by combination of hydrothermal synthesis, ultrasonication, vacuum filtration and laser irradiation,⁴⁹ and rGO- V_2O_5 /graphene–vanadium nitride (VN) based PC-MSCs fabricated by combining hydrothermal synthesis, 3D printing and vacuum freeze-drying.⁸³ This indicates the Mo@V- $\text{VO}_{0.2}$ based PC-MSCs manufactured by WEDM technique achieved excellent capacitive properties at ultra-fast charging/discharging rate. It needs to note that this remarkable performance was obtained without any help from additional conductive media and other processing techniques. Fig. 8d showed that 80AMSCs3 achieved the larger capacitance value compared to the 60AMSCs3 and 100AMSCs3, and these results were consistent with those presented at Fig. 7. This phenomenon furtherly verified that the processing voltage has a great impact on the electrochemical properties of Mo@V- $\text{VO}_{0.2}$

based PC-MSCs. The Mo@ $\text{VO}_{0.2}$ particles with relatively sparse distribution prepared by 60 V or with large agglomeration prepared by 100 V could not provide sufficient active sites for energy storage, which resulted in their relatively low capacity. The Mo@ $\text{VO}_{0.2}$ particles prepared by 80 V showed dense and uniform distribution, which facilitated more active sites for charge storage. Therefore, WEDM demonstrated its advantage in fabricating MSCs with customized performance by tailoring the surface morphology through its processing voltage.

Fig. 6S† showed the GCD images of Mo@V- $\text{VO}_{0.2}$ based 60AMSCs3, 80AMSCs3 and 100AMSCs3. Compared to those of 60AMSCs3 and 100AMSCs3, the Mo@V- $\text{VO}_{0.2}$ based 80AMSCs3 obtained relatively longer discharge time indicating better capacitive performance, which agreed well with those obtained by CV curves (Fig. 7 and 8). As depicted in Fig. 9a, the Mo@V- $\text{VO}_{0.2}$ based 80AMSCs3 showed small capacity decay and maintained a good capacity retention of 64.7% at 0.25–2 mA cm^{-2} . In addition, the device demonstrated small capacity decay of 5.6% after 2000 cycles, which furtherly verified the good cycling stability of Mo@V- $\text{VO}_{0.2}$ based 80AMSCs3 fabricated by one-step WEDM technique (Fig. 9b). This is due to the 3D binder-free V- $\text{VO}_{0.2}$ integrated electrode design, surface morphology tailoring, Mo doping, introduction of oxygen vacancies and polyvalent state of $\text{VO}_{0.2}$, which accelerates the electron/ion transportation efficiency and fully utilizes the advantage of the high capacitance of $\text{VO}_{0.2}$ active material. Most importantly, the high-performance 3D Mo@V- $\text{VO}_{0.2}$ based devices with customized electrochemical properties are prepared by a simple WEDM technology, without any help from

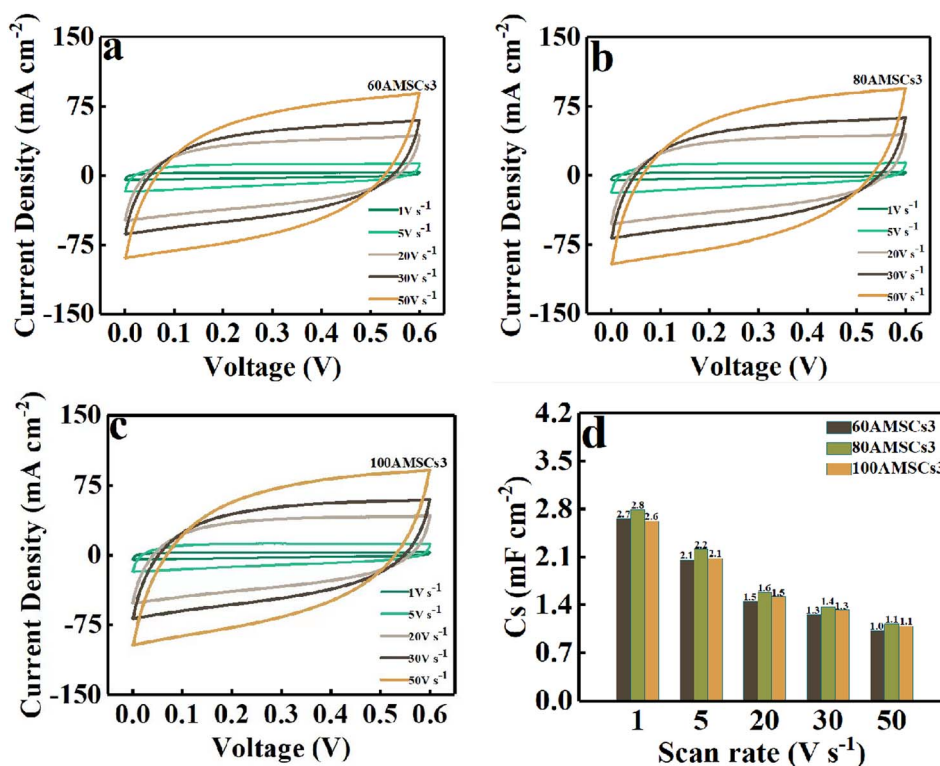


Fig. 8 CVs for (a) 60AMSCs3, (b) 80AMSCs3, (c) 100AMSCs3 at 1–50 V s^{-1} and (d) corresponding capacitance derived from CV profiles.



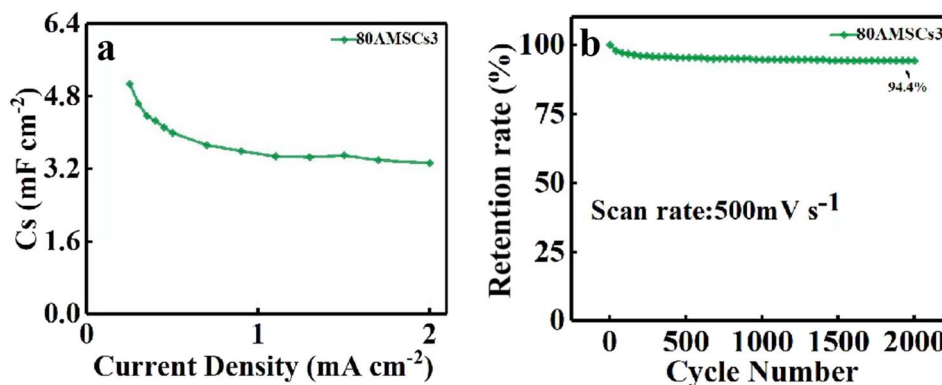


Fig. 9 (a) Corresponding capacitance derived GCD profiles and (b) the capacitance retention of 80AMSCs3.

additional conductive additives, templates, adhesives, expensive equipment, toxic solvents and other fabricated techniques. The developed WEDM manufacturing technique in this work provides a new way for scalable synthesis of metal oxide based materials and manufacturing of different energy storage devices with customized electrochemical performance.

4. Conclusion

In conclusion, a simple, safe, inexpensive, non-toxic, template-free, binder-free, environmentally-friendly and computer-aided design technique of WEDM has been developed for manufacturing arbitrary patterns of 3D Mo@V-VO_{0.2} based microdevices with customized electrochemical properties. The geometric structure of the microdevices was optimized *via* theoretical simulation and experiments. It was found that reduction of electrode width is beneficial for accelerating the ion transport rate. Moreover, the capacitive performance of Mo@V-VO_{0.2} based devices was optimized by WEDM processing voltage, which could directly tailor the surface morphology and particle distribution. Compared to 60AMSCs3 and 100AMSCs3 devices, 80AMSCs3 achieved a higher capacitance of 25.2 mF cm⁻² (at 1 mV s⁻¹). This is because the Mo@VO_{0.2} particles prepared by the processing voltage of 80 V are dense and uniform, providing more active sites for energy storage and thus enhance its electrochemical performance. Moreover, this 80AMSCs3 presents a quasi-rectangle CV shape up to 50 V s⁻¹ and achieves a superior cyclic stability of 94.4% (2000), benefiting from the 3D binder-free V-VO_{0.2} integrated electrode design, surface morphology tailoring, Mo doping, introduction of oxygen vacancies and polyvalent state of VO_{0.2}, which accelerates the electron/ion transportation efficiency and fully utilizes the advantage of the high capacitance of VO_{0.2} active material. This WEDM technique opens a new, simple, low-cost and high-precision strategy for synthesizing various metal oxides and constructing high-efficiency energy storage devices with customized performance for broad applications.

Conflicts of interest

There are no conflicts to declare.

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