FLEXIBLE HARSH ENVIRONMENT MICRO SUPERCAPACITORS USING DIRECT-WRITE 2D TRANSITION METAL CARBIDES

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ABSTRACT

2D transition metal carbides (MXenes) materials have drawn great interests for supercapacitor applications due to their unique properties, such as metallic conductivity and large specific surface areas. However, it is rather difficult to fabricate MXenes by using the process from the MAX phase, which requires a high temperature and HF etching processes. Here, we demonstrate a direct-write and fast conversion of molybdenum carbide from the Mo ions polymer composite on top of a flexible polymer substrate by an infrared laser beam. XRD results validate that the material is successfully converted to Mo3C2. The as-converted Mo3C2 has highly porous, 3D sponge-like structure generated by the localized heating effects. Preliminary testing results show that a micro supercapacitor using as-fabricated Mo3C2 as electrodes has a high measured specific capacitance of 50 F/g. Electrochemical tests of flexible micro supercapacitors at both low and high temperatures from -20 to 300°C have shown repeatable and stable performances. This laser conversion method has great potential for ultra-fast and low-cost synthesis of transition metal carbides material and the Mo3C2-based micro supercapacitor provides a promising alternative for harsh environment applications.

KEYWORDS

Flexible, micro supercapacitor, laser direct-write, molybdenum carbides, harsh environment

INTRODUCTION

Recently, a new class of 2D transition metal carbides (MXenes) material has been demonstrated to provide high specific capacitance for a new type of pseudocapacitance materials [1,2]. MXenes offer good metallic conductivity, hydrophilic surfaces and large surface area for supercapacitor applications with high performances [3]. In addition, these transition metal carbides, such as molybdenum carbide, have a melting point as high as 2500K, which make them ideal materials in harsh environmental applications, especially as the electrodes in high temperature environments [4]. The ceramic and pseudo-capacitance nature of these materials could have great potential for energy storage applications in harsh environments. However, problems in complicated synthesis process and the resulting fragile flakes have hindered their full potential. Specifically, to fabricate MXenes from the MAX phase, the process temperature is as high as 1600 °C with required HF etching processes afterwards [5,6], which is not only cumbersome but also brings safety concerns. Also, MXenes flakes are easily to restack, resulting in reduced specific surface area [7]. In addition to the traditional CVD methods and material carbonization approach, high power heating is a new scheme to pyrolyze polymer to carbon materials such as using laser to convert PEI to graphene [8-10]. In this work, transition metal carbides materials are converted by the laser ablation process based on the high local temperature generated on the laser pulses. It has the feasibility to introduce nanoscale porosity to enhance the performances of systems such as energy conversion and energy storage applications.

In this paper, we demonstrate a simple fabrication process by using laser to speedily convert the ions/gelatin solution to molybdenum carbide. After the spin-coating process on a flexible substrate, the solution is cured by an infrared laser to achieve the fast synthesis process of the carbide material. In addition, a Computer Aided Design (CAD) tool could be utilized to pattern the as-synthesized molybdenum carbide. Compared to the state of the art on the synthesis processes, our direct-write method of molybdenum carbide with an infrared laser beam is convenient and it introduces nanoscale porosity in molybdenum carbide, resulting in a high specific capacitance. In this work, a flexible micro supercapacitor is demonstrated, using the laser-converted molybdenum carbide as the electrode material to work in a wide temperature range. These Mo3C2-based micro supercapacitors exhibit high specific capacitance of 50 F/g with a wide operation range from -20 to 300°C.

FABRICATION

Figure 1 illustrates the fabrication process and prototype structure of flexible supercapacitors with interdigitated electrodes. The Kapton tape is used as the flexible substrate as it remains stable across a wide range of temperatures from −269 to 400°C. The mixture of MoCl₅ and gelatin is dissolved in DI water with 30 wt%
concentration of ethanol to form the polymer solution. The polymer solution is spin-coated onto the Kapton tape substrate and cured at 80°C for 1 hour to form a thin film of 20 μm in thickness. Then, the as-prepared sample is processed by an infrared laser with a power of 0.5 to 8 Watts and scanning speed of 150 to 400 mm/s to convert the Mo⁵⁺ ions with gelatin film to molybdenum carbides. Such infrared laser has the continuous wavelength of 10.6 μm with a micro-meter resolution, which enables the capability of direct fabrication of the interdigitated electrodes structure for flexible micro supercapacitors. In addition, a CAD software is used to design the electrode pattern and control the fabrication process parameters, which makes it possible for further mass production. After the laser ablation process, the unconverted polymer film is rinsed out of the substrate by DI water. Finally, a mixture of 5% PVA (Poly(vinyl alcohol)) and high concentration of Li⁺ ion (20 M) is used as electrolyte for harsh environment micro supercapacitors.

Figure 1: (left) Illustration of the micro supercapacitor fabricated by the laser beam by the local heating process to pattern and convert the gelatin trapping Mo⁵⁺ ions to molybdenum carbides. (Center) SEM image of laser converted Mo₃C₂ showing highly porous structures. (right) Close-up SEM photo showing the 2D flake structures.

The micro supercapacitors with Mo₃C₂–based electrodes patterned on a Kapton tape substrate are highly flexible as shown in Figure 2. The fabricated device can be wrapped around a human finger or twisted by two fingers without damaging the electrodes and their functionalities in the supercapacitors.

Figure 2: The Mo₃C₂ patterned electrodes are patterned on top of a Kapton tape showing good flexibility by wrapped around a human finger or twisted by two fingers.

CHARACTERIZATION

The as-prepared sample is examined by the scanning electron microscopy (SEM, FEI Nova NanoSEM 650), as shown in the center and right of Figure 1. The portion ablated by the laser shows the high porous, 3D sponge-like structure after the fabrication process with many flakes generated by the localized heating effects of the infrared laser beam (10.6 μm). During the laser process, the transition metal ions and polymer can absorb the IR laser energy, which results in a high local temperature up to 1700 °C within a very short time of several micro seconds [11]. The solvent with transition metal ions and polymer at the laser-focused spot can vaporize instantaneously, which generates nanoscale porosity and carbonizes the metal/gel template simultaneously. In addition, since polymer can be converted to graphene by laser ablation [10], there is some converted graphene from parts of the gelatin in the film.

X-ray diffraction (XRD) is also conducted on the Bruker D8 to examine the converted results of samples processed with different laser powers of 2, 4 and 8W. As shown in Figure 2, the characteristic peaks of the molybdenum carbide imply that the cured film has been successfully converted to Mo₃C₂ and the short amorphous carbon peak corresponds to a high yield rate of Mo₃C₂.

Figure 3: XRD results verifying the laser converted material as Mo₃C₂.

Laser ablation of Molybdenum carbide shows the power tolerance at a wide range from 0.5W to 8W. The conversion from Mo⁵⁺ ions to Mo₃C₂ will not happen
with the laser power less than 0.5W due to insufficient energy for heating, while larger laser power results in larger ablation spot that will reduce the pattern resolution. To achieve the best conductivity of as-patterned Mo₃C₂ supercapacitor electrodes, the optimized laser parameters are characterized as a power of 2W and scanning rate of 250 mm/s. The optimized solution recipe is MoCl₅ with a concentration of 2 mol/L, gelatin with 60 wt% of concentration and ethanol with 30 wt% of concentration. The converted electrode shows a low electrical resistivity around 50 Ω.□

EXPERIENMENTS AND RESULTS

Experiments on Mo₃C₂ as the electrode material as well as the as-fabricated micro supercapacitor prototype have been conducted to test their performances as well as the device stability in harsh temperature environments. The cyclic voltammetry (CV) test is used to analyze the specific capacitance of Mo₃C₂ as the electrode material using a Gamry workstation. The specific capacitance value is determined by the area integration under the obtained CV curve [12]. Using a 0.5 M H₂SO₄ as the electrolyte, the measured Mo₃C₂ supercapacitor electrode has a good specific capacitance of 50 F/g (scan rate 1mV/s), as shown in Figure 4.

The cyclic CV test of Mo₃C₂ supercapacitor electrodes was carried out with scan rate of 1000mV/s. It is observed in Figure 5 that such electrode material achieves a good cycling life of more than 10,000 cycles. The nature that transition metal caribdes have good stability to maintain their properties in a wide temperature range enables the Mo₃C₂-based micro supercapacitors to operate in a wide temperature range by using a 5% PVA and 20M Li+ as the electrolyte. The performance of Mo₃C₂-based micro supercapacitor was tested at different temperatures from -20°C to 300°C. Testing conditions with varying temperatures were calibrated with an infrared thermometer gun. Each test was carried out after the temperature has been stabilized for 10 minutes. CV curves of the as-fabricated supercapacitor were measured with a scan rate of 100mV/s. As shown in Figure 6, the area under CV curves barely changes when the temperature is lower than the room temperature and increases dramatically by further increasing the operation temperature. Compared with the room temperature condition, specific capacitance of the micro supercapacitor maintains at about more than 70% values as compared with the results at -20°C and its specific capacitance is also enhanced as the temperature increased. It is believed that Mo₃C₂ intercalated with the Li+ electrolyte has good thermal stability. Under low temperature conditions, the electrolyte ions stay inactive, leading to similar performance of the micro supercapacitor at -20°C and -10°C. The improvement of specific capacitance with respect to temperature may be attributed to the enhancement of the mobility of the ions in the electrolyte as temperature increases.

Figure 4: CVs of the laser-patterned molybdenum carbide electrodes with different scan rates.

Figure 5: The cyclic CV tests of Mo₃C₂ showing good cycling life of more than 10,000 cycles (scan rate of 1000mV/s).

Figure 6: CV tests of the micro supercapacitor with interdigitated Mo₃C₂ electrodes under a scan rate of 100 mV/s at different temperatures from -20 to 300°C.

To demonstrate the thermal stability of the Mo₃C₂ as the electrode material, another graphene-based micro supercapacitor was fabricated and tested in the same harsh environment condition for comparison. Such graphene-based micro supercapacitor employs graphene as the electrode material, which is also induced by the...
laser direct-write laser processing method [10]. The graphene-based micro supercapacitor also has the same interdigitated electrode structures, which were patterned by using a CAD software. The same electrolyte was utilized in both graphene- and Mo$_3$C$_2$-based micro supercapacitors for tests from -20 to 300 °C and both of them exhibited good tolerance to operate below 0 °C. However, after the high temperature tests at 300 °C, the Mo$_3$C$_2$-based micro supercapacitor is still intact and functional, as shown in Figure 7(a); while the micro supercapacitor with laser converted graphene electrodes has degraded and its two electrodes have shorted and been irreversibly damaged, as shown in Figure 7(b). This test result suggests that Mo$_3$C$_2$ plays an important role in the device stability for high temperature environment.

Figure 7: (a) The Mo$_3$C$_2$-based micro supercapacitor is intact; while (b) the micro supercapacitor with laser converted graphene-only electrodes degrades after high temperature tests at 300 °C

Furthermore, thermal cycling test was carried out by first raising the temperature from room temperature (25 °C) to 300 °C for 30 minutes and then lowering the temperature from 300 °C back to room temperature. The CV measurement results at room temperature before and after the harsh environments tests at 300 °C show that the capacitance can return back to its original values for stable and repeatable harsh environment operations, implying that there were no irreversible damages to both electrode and electrolyte at such a high temperature.

CONCLUSIONS

In this paper, a laser-based direct-write method is introduced to synthesize molybdenum carbides from ions/gelatin solutions for the first time. Through laser ablation process, high local heating effect could contribute to the generation of a highly porous structure, which could greatly enlarge the specific surface area. A flexible micro supercapacitor with interdigitated Mo$_3$C$_2$ electrodes has been demonstrated using this method. Testing results indicates that the micro supercapacitor has a high specific capacitance of 50F/g with cycling life of more than 10,000 cycles. By employing a 5% PVA and 20M Li$^+$ ion as the electrolyte, such Mo$_3$C$_2$ based micro supercapacitor exhibits excellent performance in harsh environments for low and high temperatures of -20 to 300°C. The direct-write laser process is performed in the ambient environment using a CAD software for scalable and low-cost manufacturing. The Mo$_3$C$_2$-based micro supercapacitor that can be used as a flexible device for energy storage applications in harsh environment is a preliminary example.

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