Laser-assisted growth of hierarchically architectured 2D MoS$_2$ crystals on metal substrate for potential energy applications

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Abstract

Recently, there has been substantial interest in the large-scale synthesis of hierarchically architectured transition metal dichalcogenides and designing electrodes for energy conversion and storage applications such as electrocatalysis, rechargeable batteries, and supercapacitors. Here we report a novel hybrid laser-assisted micro/nanopatterning and sulfurization method for rapid manufacturing of hierarchically architectured molybdenum disulfide (MoS$_2$) layers directly on molybdenum sheets. This laser surface structuring not only provides the ability to design specific micro/nanostructured patterns but also significantly enhances the crystal growth kinetics. Micro and nanoscale characterization methods are employed to study the morphological, structural, and atomistic characteristics of the formed crystals at various laser processing and crystal growth conditions. To compare the performance characteristics of the laser-structured and unstructured samples, Li-ion battery cells are fabricated and their energy storage capacity is measured. The hierarchically architectured MoS$_2$ crystals show higher performance with specific capacities of about 10 mAh cm$^{-2}$, at a current rate of 0.1 mA cm$^{-2}$. This rapid laser patterning and growth of 2D materials directly on conductive sheets may enable the future large-scale and roll-to-roll manufacturing of energy and sensing devices.

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Keywords: 2D materials, laser manufacturing, laser patterning, energy applications, Li-ion battery

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1. Introduction

Transition metal dichalcogenides (TMDCs) have recently emerged as a significant class of layered materials with a number of applications in electronics, photonics, energy storage, catalysis, and sensing devices [1–11]. The chemical composition of TMDCs has been expressed by \( \text{MX}_2 \) (\( M = \) transition metal, and \( X = \) chalcogen), where the transition metal is sandwiched in between chalcogen atoms forming a three-atom thick two-dimensional (2D) crystalline layer. The bulk structure of the TMDCs consists of repeating layers with weak van der Waals bonding between the layers and strong covalent interaction within the layers [12–15].

Among various areas of application, energy applications such as catalysis, energy generation, and storage have been promising areas of interest for 2D TMDC materials [16–21]. For instance, in lithium cells, transition metal sulfides (TMSs) have been important cathode materials [16, 22–24] where the lithium is stored in their lattices by the intercalation/deintercalation processes. Molybdenum disulfide (MoS\(_2\)) is one of the promising electrode materials, among the TMSs, for rechargeable lithium-ion batteries [23, 25–28]. The layered structure of MoS\(_2\) allows foreign molecules or ions to easily move between the layers through the intercalation/deintercalation processes [29–34].

Mono and few-layer TMDC nanosheets can be synthesized by bottom-up atom-by-atom growth processes or top-down mechanical and chemical exfoliation of bulk 2D materials [22, 35–38]. In the bottom-up atom-by-atom method, TMDCs are typically grown on different substrates (e.g., \( \text{S}/\text{SiO}_2 \)) using physical or chemical vapor deposition methods [39, 40]. In the top-down method, stacked layers are separated into few-layer sheets using chemical and micromechanical cleavage methods [41]. The bottom-up atom-by-atom approach is a low yield, high cost, and time-consuming process, which is typically used for electronic and optoelectronic applications. For instance, there are some reports on industrial atomic layer deposition (ALD) and chemical vapour deposition (CVD) approaches for the wafer-scale depositions of TMDC’s [42, 43]. The top-down mechanical and chemical exfoliation approach produces large-scale, low-cost, and fast 2D materials that are suitable for energy applications. However, mechanical and chemical exfoliation requires post-processing, slurry formation, patterning, and deposition onto conductive electrodes with reliable contact between 2D materials and metal substrates [44–47]. Therefore, large-scale, high yield, and low-cost direct synthesis approach with control over their structures, patterns, and interfaces are highly desired to manufacture 2D-based electrodes for energy applications.

Lasers applications in the synthesis and processing of 2D and other related energy materials has been an attractive area for large-scale, roll-to-roll, and low-cost manufacturing of energy devices [48–55]. Recently, laser processing has become an attractive tool for enhancing manufacturing and improving battery performance. For instance, laser modification or ablation of electrode materials is now used to create various patterns and structures on the electrodes of the batteries [56–60]. This has directly influenced the electrochemical properties and greatly enhanced battery performance, including battery lifetime, high-rate capability, and cycle stability. One of the critical issues for thick film and high energy electrodes is improving the electrode film adhesion, which can be possible by laser structuring [61–63]. Hence, a new battery concept has been introduced by the direct laser structuring of electrodes for achieving large-area energy capacities and power densities [64–67].

The wide choice of lasers with various power, energy, and timescales (from continuous-wave to femtoseconds) has enabled their use in many industrial-scale manufacturing sectors for rapid (e.g., a few thousand mm s\(^{-1}\)), high precision, and low-cost processing needs. Accordingly, this work presents the use of laser processing for rapid laser patterning and large-scale manufacturing of 2D materials with high-quality and high growth rate directly on conductive transition metals sheets. This method has the potential to be adopted in the future roll-to-roll industrial level energy device manufacturing. Besides improving the quality and growth rate, this method offers large-scale rapid manufacturing of 2D materials directly on the conductive transition metal substrates for future roll-to-roll industrial level energy device manufacturing. Here, we report a unique solution for the formation of designed patterns and hierarchically architectured high-quality 2D MoS\(_2\) crystals directly on molybdenum substrates to design electrodes for 3D batteries. This process combines the flexibility and advantages of the laser structuring method to create micro/nanostructures on molybdenum substrates, followed by sulfurization and the growth of high-quality MoS\(_2\) crystals in the patterned structures. The laser micro/nanopatterning provides the ability to design desired architectures and channels on the substrates and highly enhances the sulfur diffusion and crystal growth kinetics resulting in high yield growth of 2D crystals. Moreover, since the 2D crystals grow directly from and penetrate into the conductive substrate (Mo), there is a natural chemical bond between the 2D material and the substrate that eliminates the use of a binder for adhesion. Thus this method could be more resilient to bending. We show that the crystals are, in fact, pure with the desired quality and with suitable battery performance characteristics.

2. Results and discussion

2.1. Growth of hierarchically architectured 2D MoS\(_2\) crystals

As shown in figure 1, to create designed patterns with controlled architectures and dimensions, molybdenum substrates (99.9% purity) were precisely laser structured (see Supplementary data) in an argon environment to avoid unwanted chemical reactions and oxidation. The laser-structured substrates were then controllably sulfurized inside a tube furnace under atmospheric argon pressure and at various temperatures. After loading the samples and sulfur boat into the tube furnace, first, the tube was vacuumed down to \(~1\) mtorr, followed by argon purging for a few minutes. Then the tube was filled with 500 mtorr of argon, and the sulfurization processes were studied under various temperatures (e.g., 400 °C–900 °C) and time. The sulfurization was achieved by evaporating 10 mg
of sulfur powder in the low-temperature zone of the furnace. The furnace temperature helps dissociate the vaporized sulfur molecules to smaller chemically activate S species. The large sulfur molecules such as $S_6$, $S_7$, and $S_8$ are the dominant species in the vapor at low temperatures of about 150 °C. However, at relatively temperatures above 500 °C, the smaller molecules such as $S_4$, $S_3$, and $S_2$ become dominant [68, 69]. Therefore, the sulfur vapor close to the samples zone are expected to be a highly reactive smaller species that can diffuse into the molybdenum substrate and form MoS$_2$ structures.

In order to verify the temperature effect on the formation of MoS$_2$ crystals, different sulfurization temperatures ranging from 400 °C to 1000 °C were tested. The surface morphologies and physical structures of the synthesized MoS$_2$ samples were studied using a profilometer (see Supplementary data) and scanning electron microscopy (SEM). As shown in figure 2, the SEM images of the samples revealed a popcorn-like growth evolution of the MoS$_2$ crystals as a function of substrate temperatures. When the temperature increases, sulfur species highly react with Mo and diffuse far inside the microstructures. Since the density of Mo is almost twice the density of MoS$_2$, the MoS$_2$ will need twice the space of Mo. Thus, it begins to crack the microstructure and expand outward.

For instance, the initial sign of MoS$_2$ growth was observed at 400 °C. As the temperature was increased for a constant reaction time of 10 min, molybdenum structures started cracking, and larger MoS$_2$ flakes started springing out. At 700 and 800 °C large flower-like MoS$_2$ crystals were formed, covering the entire structure. The higher sample temperatures (i.e. 900 °C and 1000 °C) provided both higher thermal energy for diffusion during the sulfurization process and increased the reactive S species resulting in the enhanced growth of the crystals. The growth was so high that the microstructures and microchannels on the substrates disappeared. However, signs
of decompositions and degradation of MoS$_2$ crystals were observed in TEM images (see Supplementary data) when the temperature was increased to 900 °C and beyond.

The micro/nanostructures formed by the laser processing significantly increase the surface area for sulfur interaction and diffusion, leading to more sulfurization and MoS$_2$ growth than in unstructured regions. To show how laser structuring makes a huge difference in the sulfurization and enhanced growth of MoS$_2$ crystals and confirm our hypotheses, we compared the growth of MoS$_2$ crystals on both laser-structured and unstructured molybdenum substrates side by side. To perform this experiment, half of a molybdenum substrate was laser patterned, and the other half was kept intact. The sample was then loaded into the tube furnace, and MoS$_2$ growth was performed at 800 °C. As shown in figure 3, the laser-structured regions showed a much higher growth rate than the unstructured region. The unstructured region only formed a few-layer coating on the surface, while the laser-structured region experienced enhanced growth with flower-like structures.

To assess the quality and structure of the synthesized MoS$_2$ crystals at different temperatures, samples were carefully characterized by Raman spectroscopy and x-ray diffraction (XRD), as shown in figure 4. The Raman spectra of the MoS$_2$ crystals (figure 3(a)) prepared at different temperatures clearly showed the in-plane (E$_{2g}^1$) mode at 383 cm$^{-1}$ and an out-of-plane (A$_{1g}$) mode at 407 cm$^{-1}$. The interval between the E$_{2g}^1$ and A$_{1g}$ peaks was about 24 cm$^{-1}$, similar to the reported value for the bulk MoS$_2$ crystals. By increasing the growth temperature, the difference between E$_{2g}^1$ and A$_{1g}$ peaks gets larger, indicating the formation of thicker layered structures at higher temperatures [12, 70]. The asymmetric and broad peaks at 454 cm$^{-1}$ is due to the superposition of the first-order optical phonon A2u and second-order 2LA(M) vibrational modes [71, 72]. The intensity of the peaks increased for higher temperature samples, possibly due to the higher density of MoS$_2$ crystals grown at higher temperatures, as also confirmed by the SEM. At lower temperatures, since the MoS$_2$ growth is much less and slightly covers the samples’ surface, the Raman intensity was not as strong as the high-temperatures grown samples.

As shown in figure 4(b), the MoS$_2$ crystals at higher temperatures (≥600 °C) show a strong diffraction peak at 2θ = 14.4° corresponding to the (002) face, indicating the multilayer nature of the structures. As the temperature increases, this peak becomes stronger, which means the number of layers has increased. Besides, other smaller peaks located at 2θ = 32°, 39.5°, 58°, and 60.2° can be observed, which are assigned to the (002), (100), (103), (110), and (008) face, respectively (Joint Committee on Powder Diffraction Standards (JCPDS) 37-1492). If the material is monolayer or too thin, XRD typically does not show any peaks since constructive interference cannot be formed. Also, as the temperature goes up, molybdenum peaks (at 2θ = 40.6°, 58.5°, 73.7°) disappear due to increased MoS$_2$ thickness. Figures 4(c) and (d) compare the Raman and XRD spectra of the sample grown at 800 °C with and without laser structuring. The corresponding MoS$_2$ Raman peaks at 383 and 407 cm$^{-1}$ (figure 4(c)) and diffraction peak at 2θ = 14.4° (figure 4(d)) show much stronger intensity than the unstructured samples due to the higher growth of the structured regions compared to the unstructured.

To gain atomistic information regarding the quality and structure of the synthesized MoS$_2$ crystals, scanning transmission electron microscopy (STEM) images we obtained and analyzed. Figure 5 shows the STEM images of stacked MoS$_2$ crystals synthesized at 800 °C that clearly shows the layered nature of the material formed by a number of monolayers attached together via van der Waals forces. The hexagonal atomic arrangement of the Mo and S atoms is observed, confirming the 2H crystalline phases of the crystals, as shown in figure 5(b). The fast Fourier transform (FFT) pattern (inset in figure 5(b)) taken from this monolayer crystal shows a hexagonal pattern corresponding to MoS$_2$ crystals as expected. Moreover, figure 5(c) shows the close-up view of the atomic arrangements with well-defined hexagonal symmetry. The brighter spots are Mo atoms, and the dimer spots are two sulfur atoms lined up on top of each other. This is further confirmed by the intensity profile of the crystals, as shown in figure 5(d). It should be noted that, according to the STEM images, samples grown at a higher temperature (e.g. 900 °C) showed a minor sign of decomposition at the edges of the flakes (see Supplementary data).
Figure 4. Raman (a) and XRD (b) spectra of the grown MoS$_2$ structures on Mo samples demonstrating the evolution of the MoS$_2$ crystals at various growth temperatures. Comparison of the Raman (c) and XRD (d) spectra of the MoS$_2$ samples grown at 800 °C on laser-structured (blue) and unstructured (red) molybdenum surfaces.

Figure 5. STEM characterization of the synthesized MoS$_2$ crystals. High magnification STEM images (a), (b) and FFT of the crystal (inset in (b)) showing highly crystalline layered materials with hexagonal crystal structures as expected for MoS$_2$. Close-up view (c) and the intensity line profile (d) showing Mo and 2S atoms in the crystals.

2.2. Electrochemical performance in a rechargeable Li-ion battery

The preliminary studies of electrochemical properties of structured MoS$_2$ crystals were performed using electrodes fabricated on 10 mm diameter Mo substrates. The weight of the synthesized MoS$_2$ crystals on the cells was measured by weighing the samples after the laser structuring and sulfurization processes (three times for each sample) with 1 µg measurement accuracy. The differences in the measured weights were basically the amount of sulfur added to the substrate during the formation of MoS$_2$ crystals. Since there are two sulfur atoms for each Mo atom in a unit formula of MoS$_2$, and considering the atomic mass of Mo and S, it was possible to estimate...
Figure 6. Electrochemical measurements of the fabricated MoS$_2$ electrodes. (a) CV curves for the first 75 cycles at a scan rate of 0.2 mV s$^{-1}$. (b) GCD curves of the MoS$_2$ electrode fabricated at different heat treatment temperatures. (c) Discharge capacities of electrodes with laser structuring heat-treated at 600 °C, 700 °C, and 800 °C, and unstructured electrodes heat-treated at 700 °C. EIS of MoS$_2$ electrodes at different sulfurization temperatures (d) without and (e) with laser structuring. (f) EIS of laser-structured and unstructured electrodes at 800 °C.

The electrochemical properties of hierarchically architec-
tured MoS$_2$ crystals and the potential of fabricated films as electrodes for Li-ion batteries or Li-ion capacitors were invest-
gigated by studying the behavior of the electrodes during the electrochemical intercalation of Li ions. We hypothesized that the processing conditions would impact the electrochem-
ical properties of the MoS$_2$ films by affecting the electrodes’ surface area and the diffusion path of Li ions. As shown in figure 6(a), the first discharge cycle of the cyclic voltammetry (CV) test showed two peaks, similar to the corresponding galvanostatic charge/discharge (GCD) curves (figure 6(b)). As previously reported, the peak observed at 1.1 V is due to the Li-ion insertion reaction forming Li$_x$MoS$_2$, and the peak at 0.6 V is related to the MoS$_2$ conversion reaction (transformation from trigonal prisms to an octahedral phase) [27, 73, 74]. These peaks on the discharge curve disappear in the following cycles, and a peak corresponding to the insertion of Li ions into the layered MoS$_2$ appears at around 1.9–2.1 V. The peak at 2.3–2.4 V in the charge curve corres-
dents to the Li extraction from the structure of layered MoS$_2$ [74]. Figure 6(b) shows the (GCD behavior of the fab-
ricated cells with laser-structured MoS$_2$ electrodes fabricated at different temperatures. Similar voltage profiles of differ-
ent samples for the first discharge cycle at the low current density of 50 mA cm$^{-2}$ indicate similar electrochemical characteristics, with two discharge plateaus at around 1.1–1.4 V and 0.6 V, in agreement with previous reports [75–77]. In addition, the voltage profiles of laser-structured samples at 700 °C, at different current densities are shown in figure S5.

Samples fabricated at different temperatures were gal-
vanostatically cycled at different current densities. The res-
ults of cycling tests of various electrodes are presented in figure 6(c). Comparing the specific capacity of laser-structured vs. unstructured electrodes fabricated at 700 °C shows a sig-
nificant improvement in capacity, approximately 50%, for the laser-structured electrode. Also, the cycling performance sig-
nificantly improved (figure 6(c)), which can be attributed to the open channels between the MoS$_2$ layers and more space avail-
able for expansion/contraction of MoS$_2$ crystals during the insertion/extraction of Li ions. Similar behavior was observed for the electrodes fabricated at different temperatures with and without laser structuring (figure S6). In addition, the results presented in figure 6(c) show that increasing the heat treat-
ment process significantly increases the specific capacity of the electrodes, mainly due to the higher amount of MoS$_2$ crys-
tals formed at higher temperatures.

The enhanced electrochemical performance of laser-
structured electrodes can potentially be originated from two mechanisms. First, it can be related to the Li ion transfer paths created by laser structuring, which facilitate the transport of ions in and out of the electrodes. Indeed, the flake-like form of the 2D MoS$_2$ crystals can slow down ion transport into the bulk of the electrode, and laser structuring can significantly
shorten the ion diffusion path by providing electrolyte access to the MoS\textsubscript{2} flakes and enhancing the intercalation of Li ions between the flakes. Another possible reason is the improved sulfurization of Mo after laser structuring, as discussed above. The improved sulfurization increases the amount of the active material on the Mo substrates leading to their higher specific capacity \cite{57, 59, 78}.

Further insight into the electrochemical properties of the electrodes was achieved through electrochemical impedance spectroscopy (EIS). The data were obtained in 100 mHz to 1000 kHz frequency range at the open circuit potential and using a voltage amplitude of 10 mV. Figures 6(d) and (e) present the Nyquist plots of electrodes at various sulfurization temperatures without and with laser structuring. The almost vertical rise of the imaginary impedance (-Im(Z)) and the lower impedance values at low frequencies, in agreement with the results of other electrochemical tests, show the higher capacity and ion transport properties of the laser-structured electrodes. However, the Nyquist plots also show the appearance of semi-circle features at higher frequencies for laser-structures electrodes that do not exist for the electrodes without structuring. This semi-circle feature is associated with charge transfer resistance of the electrodes. This is because laser-structuring improves the ion accessibility of MoS\textsubscript{2} flakes, and the charge storage is based on the intercalation of the Li ions between MoS\textsubscript{2} flakes. However, for the electrode without structuring, it appears that the charge storage is limited to the surface of MoS\textsubscript{2}, and these electrodes show a more capacitive charge mechanism. This difference between the EIS behavior of the electrodes is highlighted in figure 6(f), where the Nyquist plots of the electrodes heat treated at the same temperature of 800 °C are compared. It is worth noting that figures 6(d) and (e) show that laser structuring has a more significant impact on the electrochemical performance of the electrodes compared to the heat treatment temperature.

3. Conclusion

In conclusion, we demonstrated a unique hybrid laser-assisted structuring and sulfurization method for the formation of hierarchically architectured high-quality 2D MoS\textsubscript{2} crystal directly on molybdenum substrates. This work verified that laser structuring significantly enhances the sulfurization and MoS\textsubscript{2} growth rate and enables morphological control over the synthesis of MoS\textsubscript{2} crystals. We also showed the effect of sulfurization temperatures on the formation and the quality of the MoS\textsubscript{2} crystals. The SEM images of the MoS\textsubscript{2} crystals showed a popcorn-like growth evolution as a function of sulfurization temperature. The energy storage capability of the samples was tested by preparing Li-ion cells and measuring their performance. The MoS\textsubscript{2} nanosheets show the specific capacities of 10 mAh cm\textsuperscript{-2}, at a current rate of 0.1 mA cm\textsuperscript{-2}, proving the effectiveness of laser structuring in enhancing the Li storage properties of fabricated MoS\textsubscript{2} electrodes. This rapid laser patterning and large-scale manufacturing of 2D materials directly on conductive sheets enable their application in future roll-to-roll industrial level energy and sensing device manufacturing.

4. Experimental

4.1. Laser structuring of the molybdenum surface

First, 0.5 mm thick Mo foil (0.25 mm thick, annealed, 99.95%) was cut into small disks of 10 mm in diameter and ultrasonically cleaned in acetone and methanol for 10 min. Then, the Mo disks were precisely structured by a 130 W tunable nanosecond fiber laser (SPI RedEnergy, wavelength = 1064 nm, pulse-width = 5 ns–2000 ns, repetition rate = 1 Hz–4 MHz) under argon atmosphere pressure to prevent unwanted chemical reactions and oxidation. A scanning galvanometer with an F-theta lens (∼12 μm spot size) and a designated software was used to control the laser scanning patterns. In the laser processing step, the goal was to create a deep and neat structure for proof of concept. Thus, various parameters such as power, speed, and pulse duration were tested to reach the desired ablation rates and structures. A scan speed of 1000 mm s\textsuperscript{-1}, laser power of 60–80 W, hatch distance 25 μm, and laser pulse-width of 508 ns produced the desired structured surfaces for this study. Our laser spot size diameter determined the laser processing resolution at the focal point (∼12 μm). Smaller spot sizes can push the feature sizes to lower limits. To create square patterns, vertical and horizontal lines were laser scanned on the surface with desired sizes and periodicities. For deeper structures, the laser scanning process was repeated a few times on the same pattern. After the laser structuring, samples were ultrasonically cleaned in acetone and methanol for 10 min to remove the loose laser-generated coating from the surface. It should be noted that shorter pulse-width lasers such as femtosecond and picosecond lasers could be more efficient for surface structuring and future upscaling and are worth the investigation.

4.2. Sulfurization and MoS\textsubscript{2} crystal growth

Prepared Mo samples were placed inside a 1-inch tube furnace. First, the system was pumped down to a few millitorrs and argon gas was used to purge the tube and remove the residual molecules. Then the pressure was raised to about 500 torr by backfilling argon gas into the tube. The temperature was set to the desired growth temperatures (400 °C–1000 °C). Solid sulfur granules (99.9995%) were located at the beginning of the quartz tube with the temperature of about 150 °C to slowly evaporate the sulfur. The evaporated sulfur then reaches the Mo substrates near the center of the tube furnace and reacts with Mo to grow MoS\textsubscript{2} crystals for the desired time. Finally, the system was turned off and naturally cooled down to room temperature.

4.3. Characterization

4.3.1. Raman spectroscopy. A home-built confocal Raman machine with a Horiba HR spectrometer and 1200 grooves mm\textsuperscript{-1} grating was used for optical spectroscopy.
A 50× microscope objective lens (numerical aperture (NA) = 0.75) and a 532 nm laser were used for data acquisition.

4.3.2. XRD measurements. Powder XRD (D8 Discover XRD system) was used to further verify the formation of crystalline MoS$_2$ in these experiments. Scans were conducted between 20 angles ranging from 0° to 90°.

4.3.3. STEM characterization. An aberration-corrected Hitachi HD2700 STEM working at 80 kV or 120 kV was used for imaging. The detectors inner angles were set to 70 mrad, 40 mrad and 25 mrad, corresponding to high, medium, and low angle annular dark field imaging.

4.3.4. Measurement, analysis, and Li ion storage properties. To analyze the electrochemical properties of samples, a standard coin cells (CR-2032, MTI, Richmond, CA, USA) were used. The disk-shaped MoS$_2$ samples were placed on copper current collectors and tested as working electrodes. Lithium metal foil was used for the counter and reference electrodes and a polypropylene membrane (Celgard, Inc., Charlotte, NC) was used as the separator. 1M lithium hexafluorophosphate solution in ethylene carbonate and diethylcarbonate (1.0M LiPF$_6$ in EC/DEC:50/50 (v/v)) was used as the electrolyte.

4.3.3. STEM characterization. An aberration-corrected Hitachi HD2700 STEM working at 80 kV or 120 kV was used for imaging. The detectors inner angles were set to 70 mrad, 40 mrad and 25 mrad, corresponding to high, medium, and low angle annular dark field imaging.

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Author contributions

P F designed and executed the laser processing/structuring and synthesis experiments, sample characterizations, and analysis. J O and M B performed the electrochemical tests and analysis and participated in discussions and manuscript preparation. M M S led the project, led the design of experimental, participated in the data analysis, discussions, and manuscript preparation. The authors all read and commented on the manuscript.

Conflict of interest

The authors declare no conflict of interest.

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