Tailoring Ti$_3$CNT$_x$ MXene via an acid molecular scissor

Ningjun Chen$^a$, Yihao Zhou$^b$, Songlin Zhang$^b$, Haichao Huang$^a$, Chuanfang (John) Zhang$^c$, Xiaotong Zheng$^a$, Xiang Chu$^a$, Haitao Zhang$^{a,x}$, Weiqing Yang$^{a,x}$, Jun Chen$^{b,x}$

$^a$ Key Laboratory of Advanced Technologies of Materials (Ministry of Education), School of Materials Science and Engineering, State Key Laboratory of Traction Power, Southwest Jiaotong University, Chengdu 610031, PR China
$^b$ Laboratory of Functional Polymers Empa, Swiss Federal Laboratories for Materials Science and Technology, Empa, ETH Domain, Überlandstrasse 129, CH-8600 Dübendorf, Switzerland
$^c$ Department of Bioengineering, University of California, Los Angeles, Los Angeles, CA 90095, United States

**A R T I C L E   I N F O**

Keywords:
Ti$_3$CNT, MXene
Defect engineering
Active nitrogen
Acid molecular scissor
Micro-supercapacitors

**A B S T R A C T**

MXenes are attracting growing attentions from scientific community owing to their decent electric and ionic conductivity, highly accessible surface area, and the presence of redox-active sites. Herein, an acid molecular scissor is proposed to artificially tailor Ti$_3$CNT$_x$ MXene at the atomic scale and create defective nanosheets and redox-active sites. The tailored Ti$_3$CNT$_x$ MXene exhibits a significantly improved electrochemical performance with the specific capacitance reaching 376 F g$^{-1}$ and 230.68 mF cm$^{-3}$, much higher than that of original Ti$_3$CNT$_x$ MXene (237 F g$^{-1}$ and 168.27 mF cm$^{-3}$). The tailored Ti$_3$CNT$_x$ MXene was further assembled into a micro-supercapacitor, which demonstrates a high volumetric capacitance of 250 F cm$^{-3}$, a high energy density of 12.46 mW h cm$^{-3}$ at a power density of 0.43 W cm$^{-3}$. This work offers a new strategy to reinvent MXenes at the atomic scale with largely enhanced redox-active sites for energy storage, catalysis, solid lubricants and electromagnetic interference shielding.

1. Introduction

Wearable electronics are changing our living in meaningful ways [1–4]. MXenes, with the unique intrinsic crystal structure and surface chemistry, have attracted tremendous attentions in the community. Their advantageous properties, including competitive electrical conductivity, compelling intercalation effect, fast ion diffusion and outstanding capacity [5–7], render them outstanding candidates for many innovations in different fields, such as energy [7–11], sensing [5], membrane technology [11], electromagnetic interference shielding [12] and catalysts [13–15]. Notably, the MXenes exhibited the superior electrical conductivities (12,000 S cm$^{-1}$) [16–18] and higher volumetric capacitance (1500 F cm$^{-3}$) [9] with excellent cyclability and rate performance than the metal oxides [19] and other 2D carbon-based electrodes, which is limited at around 300 F cm$^{-3}$ [20,21]. Specifically, it has been demonstrated that nitrogen-containing MXene (such as Ti$_3$CNT$_x$) have better wettability [22], conductivity [23] and higher pseudocapacitance [24] than carbon-based materials (such as Ti$_3$C$_2$T$_x$). These excellent performances profit from the lone electron pairs of the nitrogen which can supply additional negative charges in conductive networks and active sites of redox reactions.

Currently, various approaches are blooming to modify MXenes, including the doping [25] and interlayer engineering [26] to improve the capacitance performance, morphology engineering [27] to activate the catalytic activity, band gap engineering [28] to regulate the band structure, and defect engineering [29] to enhance the electromagnetic shielding performance. Defect engineering has been extensively applied to manipulate the electrical, magnetic, electrochemical and optoelectronic properties of 2D materials [30–38]. However, owing to the unique structure of MXenes, introducing controllable defects or vacancies on MXene nanosheets at atomic scale is challenging yet highly desired [39, 40]. Currently, MXenes’ defects or vacancies that are created by hydrofluoric acid (HF) solution [41] or the hydrochloric acid/ hydrogen peroxide solution [27] are uncontrollable due to the unsafe and excessive etching process in concentrated acid and oxidant solutions [7,26,27, 30,42]. Concomitantly, such a process usually weakens intrinsic properties of MXenes significantly, such as the decreased structural stability and lowered conductivity of single-layer flakes [6,30].

Herein, we proposed an acid molecular scissor to controllably and precisely tailor the Ti$_3$CNT$_x$ MXenes with designed morphology and
density of defects. The created defect sites on MXene nanosheets act as ideal platforms for proton incorporation [43]. Particularly, these sites function as channels for more unobstructed accessibility with superior diffusion and transmission ability. And the resulting MXene thin film demonstrates significantly improved electrochemical activity with a capacitance reaching 376 F g$^{-1}$, compared to 237 F g$^{-1}$ of the untailored MXene. The as-prepared micro-supercapacitors (SCs) show an areal capacitance up to 74.5 mF cm$^{-2}$ and a volumetric capacitance up to 250 F cm$^{-3}$. The molecular scissor reported in this work will reinvent the MXenes at the atomic scale with a wide range of applications in high-performance energy storage [7], catalysis [41,44], solid lubricants [45], and electromagnetic interference shielding [27].

2. Results and discussion

Our strategy is involved with the in situ formation of hydrofluoric acid, which plays the acid molecular scissor’s role to controllably tailor titanium atoms and obtain redox-active sites for pseudocapacitive reactions (strong proton intercalations in acidic electrolytes [46]), as schemed in Fig. 1a. During the tailoring process, Ti vacancy clusters ($V_{Ti}^{\delta}$) in the MXenes are formed, and the atomic arrangement in the nanosheets becomes disordered. As the extent (i.e., intensity) of acid molecular tailoring increases, the $V_{Ti}^{\delta}$ gradually merge into holes (with size beyond the atomic scale), thus, increasing the density of edge defects in the tailored MXenes. Hence, we can elegantly tailor the titanium atoms so that the adjacent carbon and nitrogen atoms are exposed to the acidic molecular scissor’s environment leading to further tailoring of carbon atoms due to the electronegativity difference of nitrogen (3.04) and carbon (2.55) atoms [47] as demonstrated in Fig. 1b-c. Overall, three kinds of active nitrogens, including pyridine nitrogen (Pyridinic-N and Pyridinic-N-O) and pyrrolidine nitrogen (pyrrolic-N) [48], appeared during the tailoring process, corresponding to Fig. 1d-f, respectively. Their pseudocapacitive reaction mechanisms are illustrated as follows:

$$T_iCN + \delta H^+ + \delta e^- \rightarrow T_iCNH_2 \tag{1}$$
$$T_iCNO_y + \gamma H^+ + \gamma e^- \rightarrow T_iCN(OH)_y \tag{2}$$
$$T_iCNO_y(OH)_{\gamma}F_z + \delta H^+ + \delta e^- \rightarrow T_iCNO_{\gamma-y}(OH)_{\gamma}F_z \tag{3}$$

Where $\delta$, $\gamma$, $x$, $y$ and $z$ are the coefficients of the corresponding atoms [24, 49]. Pyridinic-N with a lone electron pair is formed by removing one carbon atom adjacent to nitrogen as shown in Fig. 1d, which adsorbs protons and serves as landing points to realize redox reaction (Eq. (1)) [50]. In a further step, this adjacent nitrogen atom can adsorb one oxygen atom to form the dangling N=O bond with two lone electron pairs of oxygen, as displayed in Fig. 1e. Moreover, it initializes the protonation process of N-O-H in Eq. (2). Unlike pyridinic-N, the pyrrolic-N (Fig. 1f), along with a lone electron pair, is formed by acidic molecular scissors tailoring of two C atoms adjacent to nitrogen. Then under-coordinated carbon atoms will realign with nitrogen atoms. These as-obtained redox-active sites of Pyridinic-N, Pyridinic-N-O and Pyrrolic-N synergistically contribute to partial pseudocapacitance of Ti$_3$CNT$_x$ MXene through supplying additional negative charges via their lone electron pairs to absorb electrolyte ions and further promote redox reactions [51,52]. Apart from the three-nitrogen redox-active sites, pseudocapacitance is also contributed by the surface terminations (-O, -OH) (Eq. (3)). To determine accurate nitrogen contents and their species of the Ti$_3$AlCN precursor and as-prepared Ti$_3$CNT$_{24}$ h (the sample etched for 24 h) X-ray photoelectron spectroscopy (XPS) was performed on both samples, and results are shown in Fig. 1g, h, S1 and S2. Compared with the Ti$_3$AlCN precursor, Ti$_3$CNT$_{24}$ h possessed additional three species of high-activity nitrogens (Pyridinic-N, Pyridinic-N-O and Pyrrolic-N) and its nitrogen content was up to 10.94 at% (atomic number percentage). For comparison, Figs. S3 and S4 show the XPS results of Ti$_3$CNT$_{12}$ h (the sample etched for 12 h) and

Fig. 1. An acid molecular scissor for tailoring Ti$_3$CNT$_x$ MXenes. (a) Ti$_3$CNT$_x$ MXene with high-activity nitrogens partsakes pseudocapacitive progress. (b, c) Acid Molecular scissors acting on the nanosheet of MXene. (d) Pyridinic-N active site. (e) N–O active site. (f) Pyrrolic-N active site. (g) XPS N region spectra of Ti$_3$AlCN. (h) XPS N region spectra of Ti$_3$CNT$_{24}$ h enriched with multiple nitrogen active sites.
The acid molecular scissors can effectively remove the aluminum layers in the MAX phase after 12 h etching, which is confirmed by the less than 0.1 at% aluminum atomic content in the elemental mapping (Figs. S5 and S6a). Excellent uniformity of nitrogen element distribution was also verified in addition with other elements (F, Ti, O and C). The scanning electron microscopy (SEM) of obtained multilayer MXene is shown in Fig. S6b, demonstrating the typical layered structure of well-stacked Ti$_3$CNT$_x$ flakes. Transmission electron microscopy (TEM) and the corresponding selected area electron diffraction (SAED) patterns of Ti$_3$CNT$_x$ shown in Fig. S6b, demonstrating the typical layered structure of well-stacked Ti$_3$CNT$_x$ flakes. Transmission electron microscopy (TEM) image and the corresponding selected area electron diffraction (SAED) patterns of Ti$_3$CNT$_x$-12 h flakes reveal its single crystal structure with hexagonal basal lattice (Figs. S6c and S6d). Apart from the nanosheets, Ti$_3$CNT$_x$ films were also prepared via vacuum-assisted filtration and characterized accordingly. The cross-section SEM image (Figs. S6e) of the Ti$_3$CNT$_x$ film reveals the stacked nanosheets. Fig. S6f compared X-ray diffractometer (XRD) patterns of Ti$_3$AICNT precursor, Ti$_3$CNT$_x$-12 h and Ti$_3$CNT$_x$-24 h. Their nanosheet interlayer spacings (corresponding to the (002) diffraction peaks) were found to gradually increase from 1.27 nm (Ti$_3$CNT$_x$-12 h) to 1.33 nm (Ti$_3$CNT$_x$-24 h), which indicates more inserted H$_2$O molecules. It also suggests that Ti$_3$CNT$_x$-24 h should possess more unobstructed accessibility. Consequently, compared to that of Ti$_3$CNT$_x$-12 h, the superior diffusion and transmission ability of H$^+$ (0.12 nm) are expected for Ti$_3$CNT$_x$-24 h during the rapid charge-discharge process.

The acid molecular scissors strategy to tune the surface defect concentration is crucial toward controlling the surface properties of MXenes for energy, sensing, membrane technology, electromagnetic interference, catalysts and other applications. As discussed above, the defects are formed when the surface titanium atoms are etched by excessive immersion in an acidic scissor environment. High resolution transmission electron microscopy (HRTEM) images projected along the c axis of Ti$_3$CNT$_x$ flake are shown in Fig. 2a-c for a deep insight into the tailoring mechanism. Compared with the Ti$_3$CNT$_x$-12 h (Fig. 2a, S7a and S7b) nanosheets with a low concentration of titanium vacancies ($V_{Ti}$), the removal of titanium atoms is relatively common with the increase of etching time in an acidic scissor environment. For Ti$_3$CNT$_x$-24 h nanosheets, the uniformly distributed $V_{Ti}$ defects are conducive to exposing the nitrogen and carbon atoms (Fig. 2b and S7c). These defects with unique electronic structures exhibit higher redox activity to anchor foreign atoms or functionalization (i.e., protonation). When the etching time reaches 48 h, a large area of $V_{Ti}^-$ appears (Fig. 2c, S7a and S7b), causing the amorphous array of atoms in nanosheets. Therefore, the statistical error gradually increases when calculating the number of $V_{Ti}$.

Moreover, the aforementioned $V_{Ti}^-$ clusters were also found in the samples etched for 24 h (Fig. S7d), verifying the gradual tailoring extent of acid molecular scissors. We statistic all the stripped titanium atoms in tens of images, and the results are summarized in Fig. 2d. The average $V_{Ti}$ concentration is clearly correlated with the tailoring time in an acid scissor environment. The C, N atoms and the functional groups are not distinguishable because of their low scattering intensity and their overlap with the titanium atoms when acquired along the c axis. Besides, extensive defect clusters or hole fuse, and the size of nanosheets also decreases. Hence, the statistical size distribution of these three samples was analyzed. The average particle size of Ti$_3$CNT$_x$-12 h nanosheets ranges from 0.8 to 1.2 µm. After tailoring using acid molecular scissors, the average particle sizes of Ti$_3$CNT$_x$-24 h and Ti$_3$CNT$_x$-48 h were measured to be from 0.4 to 0.8 µm and approximately 0.4 µm, respectively (Fig. 2e). Compared with the neat and flawless membrane surface, the rough and fragmented membrane surface can reflect the molecular scissors effect because of the presence of the tailored small flakes by acid molecule scissors (Figs. S8a and S8b). Fig. 2f presents the Atomic force microscopy (AFM) images of monolayer Ti$_3$CNT$_x$-12 h and Ti$_3$CNT$_x$-24 h flakes. The average thicknesses of both monolayer flakes are around 1.5 nm, indicating the minimum defect effect on the height profiles of MXene flakes.
The three Ti$_2$CNT-MXene flakes were then assembled into thin films via a vacuum-assisted filtration method and tested as supercapacitor electrodes. Fig. 3a shows cyclic voltammetry (CV) curves of the Ti$_2$CNT$_x$–24 h electrode in the voltage range of –0.3 to 0.3 V, which is nearly rectangular even at a scan rate of 100 mV s$^{-1}$, indicating excellent charge storage characteristic and outstanding rate performance. In contrast, the CV curves of Ti$_2$CNT$_x$–12 h in Fig. 3b presents lower storage capacity and distorted shapes at high scan rates. Fig. 3c demonstrates the specific capacitance of all tailored samples at different scan rates. Apparently, the Ti$_2$CNT$_x$ electrode exhibits significantly improved specific capacitance at all scan rates (i.e., 376 F g$^{-1}$ vs. 237 F g$^{-1}$) and much higher capacitance retention (i.e., 76.8% vs. 35.8%) compared to the Ti$_2$CNT$_x$–12 h electrode. The Ti$_2$CNT$_x$–24 h electrode’s superior electrochemical performance is also validated by the galvanostatic charge-discharge (GCD) measurements. As plotted in Fig. 3d–f, longer charge/discharge time and higher capacitance are observed for the Ti$_2$CNT$_x$–24 h electrode. The performance difference between the Ti$_2$CNT$_x$–12 h and Ti$_2$CNT$_x$–24 h electrodes is ascribed to the fast and reversible faradic reaction of Pyridinic-N, Pyridinic-N-O and Pyrrolic-N (Eq. (1) and Eq. (2)), that were exposed on the Ti$_2$CNT$_x$–24 h surfaces brought by acid molecular scissors. This claim is further supported by the Nyquist plot in Fig. 3g, in which it is observed that the internal resistance of the Ti$_2$CNT$_x$ electrode increases with increasing tailoring time. In contrast, the charge transfer resistance demonstrates a reverse trend. Such a phenomenon can be explained by introducing more intercalated water molecules to reduce the conductivity [53] and more redox-active sites to facilitate the pseudocapacitive reaction. Additionally, the intrinsic areal capacitance ($C_A$) [54], which is ideally achieved in the absence of electron transport or ion diffusion limitations across the electrodes, and time constants ($\tau$) of the Ti$_2$CNT$_x$–24 h and Ti$_2$CNT$_x$–12 h electrodes are calculated and displayed in Fig. 3h. The $C_A$ is consistent with the corresponding measured areal capacitance. The response time of the Ti$_2$CNT$_x$–12 h electrode is 6 times longer than that of the Ti$_2$CNT$_x$–24 h electrode, providing further evidence for the high-speed ion diffusion and transport inside the defective nanosheets.

The specific capacitance of the Ti$_2$CNT electrode is positively correlated with the quantities of nitrogen inside the electrode as shown in Fig. 3i, implying that the exposed nitrogens introduced by acid molecule scissors indeed serve as redox-active sites and contribute considerably to its capacitance.

To prove the practical applications of Ti$_2$CNT-MXene as energy storage devices, we assembled the films into micro-supercapacitors (SCs) with polyvinyl alcohol/sulfuric acid (PVA/H$_2$SO$_4$) gel electrolyte (Fig. 4a–c). These as-fabricated SCs possess finger-width from 0.2 to 1 mm. Fig. 4d–f shows the corresponding CV curves at a scan rate of 5 mV s$^{-1}$, Nyquist plots and GCD curves at 1 mA cm$^{-2}$ of these SCs with

Fig. 3. Electrochemical properties of the Ti$_2$CNT$_x$ Films in H$_2$SO$_4$ (1 M) electrolyte. (a) CV curves of the Ti$_2$CNT$_x$–24 h electrode. (b) CV curves of Ti$_2$CNT$_x$–12 h electrode. (c) Specific capacitance obtained from CV curves. (d) GCD curves of Ti$_2$CNT$_x$–24 h. (e) GCD of Ti$_2$CNT$_x$–12 h. (f) Specific capacitance obtained from GCD curves. (g) Nyquist plots of all Ti$_2$CNT$_x$ electrodes. (h) Measured areal capacitance, and the corresponding intrinsic areal capacitance and time constants of Ti$_2$CNT$_x$–12 h and Ti$_2$CNT$_x$–24 h. (i) Consistent trends of nitrogen contents and specific capacitance with increasing tailoring time.
different specifications, respectively. It is observed that the performance of SCs is directly related to the widths of interdigitated fingers. The optimum capacitive performance was obtained for the SCs with a finger width of 0.4 mm, exhibiting an areal capacitance of 174.5 mF cm⁻², much higher than other specifications. During the charging process, the electrolyte ions can transport to the interior of MXene electrodes from both the top side and the edge of interdigitated fingers. When the finger-width increases from 0.4 mm to 1 mm, the capacitance of the SCs decreases because the edge side of the electrode dominates the ion diffusion. When the finger-width decreases to 0.2 mm, the ion diffusion path becomes shorter, and electrolyte ions are more comfortable to intercalate into the electrode. However, the larger internal impedance (Fig. 4e) leads to the lower discharge capacitance of the SCs (Fig. 4f). Fig. 4g presents the Ragone plots of the assembled SCs using Ti₃CNTₓ-12 h and Ti₃CNTₓ-24 h with a finger-width of 0.4 mm. Compared with the assembled SC using Ti₃CNTₓ-12 h, a higher energy density of 12.46 mW h cm⁻³ is achieved at a power density of 0.43 W cm⁻³ in the assembled SC using Ti₃CNTₓ-24 h. When the power density increases to 4.5 W cm⁻³, the SC still maintains an energy density of 10.5 mW h cm⁻³, benefiting from both the tailored surface chemistry (using the acid molecular scissors) and well-designed device structure (optimizing the finger-width). To explore the potential applications of SCs, multiple devices must be connected in parallel or series to obtain the required capacitance and voltage. Fig. 5a displays the CV of SCs connected in series at 20 mV s⁻¹. Obviously, three SCs in series enable an operating voltage of 1.8 V and a decrease of current correspondingly. The GCD curves at 10 mA cm⁻² of the tandem circuit in Fig. 5b also delivers a higher potential window than that of a single device, consistent with the CV curves. It is worth noting that the IR drop is up to 0.6 V due to the superimposed resistance, which is further confirmed by the Nyquist plot in Fig. 5c. The series circuit was further used to drive daily LED lights (2.4 V), which can maintain brightness for up to 15 s (Supporting Video S1). The two and three parallel-connected SCs enable double and triple areal capacitance (Fig. 5d) and discharge times (Fig. 5e). Their resistances can be inferred from the Nyquist plot in Fig. 5f, which yields a reciprocal relationship as expected. These encouraging results clearly demonstrate the potential of Ti₃CNTₓ MXenes tailored by acid molecular scissors for high-density energy storage applications.

Supplementary material related to this article can be found online at doi:10.1016/j.nanoen.2021.106007.

3. Conclusion

In summary, via the acid molecular scissors, the defects were precisely introduced into the Ti₃CNTₓ MXene, which exhibits a capacitance up to 376 F g⁻¹ and 230.68 mF cm⁻². The assembled supercapacitor based on the tailored MXene delivered a large volumetric capacitance of 250 F cm⁻³ and an energy density of 12.46 mW h cm⁻³ at a power density of 0.43 W cm⁻³. The acid molecular scissors reported in this work represent a controllable and constructive approach to produce defects in the MXene systems, which could reinvent MXene nanomaterials at an atomic scale and open doors to various applications in energy, sensing and therapy.

4. Experimental section

4.1. Synthesis and tailoring of Ti₃CNTₓ MXene

1 g LiF (99%, Chengdu Ke Long Co.) was added to 20 ml 9 M HCl solution (Chengdu Ke Long Co.). After that, 1.2 g Ti₃AlCN powder was slowly added into the mixture solution with stirring in 5 mins. The acid molecular scissors will etch the Ti₃AlCN precursor for 12 h, 18 h, 24 h, 36 h and 48 h, respectively. The 12-h, 24-h and 48-h etched samples are successively marked as Ti₃CNTₓ-12 h, Ti₃CNTₓ-24 h and Ti₃CNTₓ-12 h. The reaction temperature was kept at 40 ºC. The final suspension was repeatedly washed with deionized water (DI water) until the supernatant reached a pH value of 6.0. To obtain the Ti₃CNTₓ MXene colloidal solution, a further ice-bath sonication was applied at the power of 100 W for 1 h, and then centrifugation at 3500 rpm for 30 min was processed to remove the sediment. The aqueous solution was then filtered on the hydrophilic membrane with a pore size of 0.2 µm using vacuum-assisted filtration to prepare the Ti₃CNTₓ films. Finally, the Ti₃CNTₓ films were dried.
at room temperature.

4.2. Fabrication of Ti$_3$CNT$_x$ supercapacitors

Firstly, a gold-plating layer was deposited on the Ti$_3$CNT$_x$ film by magnetron sputtering (TRP450, China). This Ti$_3$CNT$_x$ film then was carved into an interdigital pattern via cold ultraviolet laser marking technology (UV-3S, China) and was glued to a PET film. PVA/H$_2$SO$_4$ gel electrolyte, which was prepared by 8 g sulfuric acid (H$_2$SO$_4$, 98%, Chengdu Ke Long Co.), 8 g polyvinyl alcohol (PVA, 1799 type) and 80 ml DI water at the temperature of 80 $^\circ$C, was slowly dropped onto the interdigital film. When the covered gel electrolyte presents semi-solidification, polydimethylsiloxane (PDMS) was employed to encapsulate the Ti$_3$CNT$_x$ micro-supercapacitor.

4.3. Material characterization

The materials were recorded by XPS with a Thermo Scientific ESCALAB 250Xi spectrometer. A JEOL JSM-7800 Prime scanning electron microscopy (SEM) with an accelerating voltage of 5 kV was conducted to measure the Ti$_3$AlCN precursor, freeze-dried powders of multilayered Ti$_3$CNT$_x$ MXenes and surface topography of Ti$_3$CNT$_x$ films. The corresponding element distribution was detected via energy dispersive X-ray spectroscopy (EDS). The as-synthesized materials were characterized by XRD (PANalytical X’Pert Powder diffractometer, Holland) with Cu Kα radiation between 5° and 80°. HRTEM, TEM and corresponding SAED (JEOL JEM-2100, Japan) patterns were used to collect their morphology and structure information. AFM (Bruker Multimode 8, American) images of the Ti$_3$CNT$_x$ nanosheets were measured to characterize nanosheets’ thickness. It is worth noting that the nanosheets measured by TEM and AFM are samples obtained by shaking and centrifuging before ultrasonic, preventing the error caused by ultrasonic damage to the nanosheets.

CRediT authorship contribution statement


Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

W. Y. and H. Z. acknowledges the National Natural Science Foundation of China (No. 51977185 and No. 51972277) and Sichuan Science and Technology Program (No. 2022YJF2478 and No. 20ZDYF2833). J. C. acknowledges the Henry Samueli School of Engineering & Applied Science and the Department of Bioengineering at University of California, Los Angeles for the startup support. The authors also would like to thank Analytical and Testing Center of Southwest Jiaotong University for their assistance with the TEM and SEM analyses. And we really appreciate the support provided by Ceshigo Research Service (https://www.ceshigo.com/) for XPS characterization. N.C. and Y. Z. contributed equally to this work. W. Y. submitted the manuscript and J.C. was the lead contact.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the

References