Improved synthesis of Ti$_3$C$_2$T$_x$ MXenes resulting in exceptional electrical conductivity, high synthesis yield, and enhanced capacitance$^\dagger$

Ali Shayesteh Zeraati,$^{a,b}$ Seyyed Alireza Mirkhani,$^a$ Pengcheng Sun,$^b$ Michael Naguib,$^c$ Paul V. Braun$^{d,*}$ and Uttandaraman Sundararaj$^{d,*a}$

For the first time, an “Evaporated-Nitrogen” Minimally Intensive Layer Delamination (EN-MILD) synthesis approach is reported to synthesize exceptionally high quality MXene sheets. In the EN-MILD method, the concentrations of acids and Li-ions are continuously increased during the etching process. By implementing the EN-MILD approach, the electrical conductivity increases up to $2.4 \times 10^4$ S cm$^{-1}$, which is the highest reported value to date for Ti$_3$C$_2$T$_x$, MXenes (a traditional MILD approach results in a conductivity of $5.8 \times 10^3$ S cm$^{-1}$). This significant improvement in electrical conductivity arises from the high quality of the synthesized MXene sheets as well as a larger flake size. The EN-MILD synthesis approach also offers high yield of delaminated single MXene layers (up to ~60% after the first round of washing/centrifugation) and high colloidal concentrations (up to 31 mg ml$^{-1}$). The working electrode prepared from free-standing MXene paper shows an exceptional capacitance of $\approx 490$ F g$^{-1}$ at 1 A g$^{-1}$ in a supercapacitor, which is among the highest values reported for MXene-based supercapacitor electrodes. The exceptional electrical conductivity, high yield of delaminated MXene single layers, and high colloidal concentration of the EN-MILD approach significantly expand the applications of MXenes.

1. Introduction

Two-dimensional (2D) nanomaterials offer interesting properties in comparison with their 3D counterparts.$^{1,2}$ They have ultra-high surface areas and mechanical flexibility, two properties of considerable interest for a range of applications.$^{3-5}$ The emergence of MXene family-transition metal carbides, nitrides, and carbonitrides as a new class of 2D nanomaterials ignited considerable interest in the research community owing to their unmatched electrical and mechanical properties.$^{6-8}$ Among the synthesized MXenes so far, Ti$_3$C$_2$T$_x$ possesses the highest electrical conductivity$^9$ and has demonstrated outstanding performance in applications such as energy storage,$^{10-13}$ sensors,$^{14-16}$ EMI shielding,$^{17-19}$ and optoelectronics.$^9$ Performance in these applications is directly related to electrical conductivity, and therefore, there is motivation to further increase the Ti$_3$C$_2$T$_x$ electrical conductivity. Ti$_3$C$_2$T$_x$ electrical conductivity strongly depends on etching protocols and etching conditions as graphically presented in Fig. 1a. Generally, two HF-based etching protocols are used for the preparation of Ti$_3$C$_2$T$_x$: direct hydrofluoric (HF) etching$^{8,20}$ and in situ HF formation method.$^{10,20,21}$ Usually, MXene flakes produced by in situ HF formation (and specifically the Minimally Intensive Layer Delamination (MILD)) have larger lateral dimensions, fewer defects and higher electrical conduc-
We introduce a modified MILD approach, Evaporated-Nitrogen Minimally Intensive Layer Delamination (EN-MILD), which minimizes oxidation and increases the acid and Li-ion concentrations during the etching stage. The synthesized MXene sheets with EN-MILD deliver an exceptionally high electrical conductivity (up to $2.4 \times 10^4$ Sc$^{-1}$m) and a high capacitance of $\sim$490 F g$^{-1}$ at 1 A g$^{-1}$ as they were used as an electrode in a supercapacitor. Employing the EN-MILD approach results in a high delamination yield and colloidal concentration that address the MXene synthesis challenges in the literature. To study how EN-MILD affects the synthesis efficiency and electrical conductivity, we systematically investigated MXene synthesis using EN-MILD approach for different etching times. This approach has significant potential to be used for MXene synthesis since it gives improved synthesis yield, a high colloidal concentration, and enhanced electrical conductivity.

2. Results and discussion

The synthesis approach described here is graphically illustrated in Fig. 1b and Fig. S1a.$^\dagger$ The MILD approach was significantly improved by purging dry nitrogen in the etching phase,
to eliminate dissolved oxygen and increase the acid and Li-ion concentrations by the controlled evaporation of the etching solution (Fig. S1†), which may improve the etching of the MAX phase. This higher acid concentration also promotes better dissolution of LiF in our protocol whose existence adversely affects electrical conductivity.34–36 The washing step is the same as the MILD washing protocol to reach pH about 6 (see Fig. S1d†). Then, the sediment was dispersed in Millipore water by 10 min of bath sonication (under dry nitrogen in ice bath) and centrifuged for 1 h to separate single layer MXene sheets from the un-etched MAX phase or multi-layer MXene sheets. The MXene content in the supernatant (after 1 h centrifugation which is mostly single layer MXene) to the initial mass of the MAX phase is defined as the yield of synthesis (delamination) in this study. Fig. 1b schematically displays the etching/intercalation improvement during the etching by the EN-MILD approach where higher acid and Li-ion concentrations are formed by evaporation of the etching solution. Fig. S1† illustrates the volume changes of etching solution for the MILD approach and EN-MILD approach after 6 to 30 h. By increasing the etching time, the volume of the etching solution decreased in our approach while it remained almost unchanged in the MILD method. For etching 1 g MAX phase, the initial volume of the etching solution was 20 ml which decreased to 19 ml and ≈10 ml after etching by MILD and EN-MILD approaches for 24 h, respectively. This change provides more HF and Li-ions resulting in a better etching performance and higher intercalation as shown in Fig. 1b. In EN-MILD approach where more HF and a higher concentration of Li-ions are achieved, more aluminum (Al) atoms are removed from the structure and better intercalation is achieved, which can improve the delamination yield of single layer MXenes. The scanning electron microscopy (SEM) images for MAX/MXene powder (after washing cycles) synthesized using different conditions are compared in Fig. 1c–h. The 3D compact structure of Ti₃AlC₂ changed to a 2D structure (platelets) when it was etched for 24 h and longer by the EN-MILD approach. This confirms the high etching efficiency of the EN-MILD approach. SEM coupled with X-ray photoelectron spectroscopy (XPS) analysis indicates the complete removal of Al from the structure after 24 h etching with EN-MILD.

Structural changes induced by different etching conditions were analyzed by X-ray diffraction (XRD). The XRD patterns of freestanding MXene films in Fig. 1i showed a set of broad diffraction peaks at 2θ of about 7.2°, 18.3°, 27.7°, and 35° respectively corresponding to (0002), (0004), (0006), and (0008) planes which are in agreement with the literature.20,21 XRD patterns of MXene films show increased interlayer spacing compared to that of the MAX phase (MXene, major peak at 2θ ≈ 7.2° corresponding to an interlayer spacing of 12.3 Å (Table S4†) compared with MAX’s peak from (0002) at 2θ ≈ 9.6° corresponding to 9.2 Å). This increase in the interlayer spacing corresponds to the etching/exfoliation of the MAX phase, the formation of functional groups on the MXene surface, and intercalated ions/water molecules in the interlayer galleries of hydrophilic MXenes.36 Free-standing MXene papers prepared from EN-MILD at 24 h and 30 h MXenes had the lowest 2θ for the (0002) plane and the highest interlayer spacing. This is attributed to more intercalated ions/water with longer etching time.36 The XRD analysis of the MAX/MXene powders (6 h and 12 h etching) after the final stage of washing is shown in Fig. S2.† As is shown, the Ti₃AlC₂ MAX phase displays a strong peak at 2θ about 39° while etching in the presence of nitrogen demonstrates a significant reduction of this peak’s intensity indicating a high removal of the Al layer even after 6 h.

Another interesting outcome of the EN-MILD approach is its high synthesis yield and colloidal concentration. As illustrated in Fig. 1j, etching the MAX phase by the EN-MILD approach led to a synthesis (delamination) yield as high as 60%, which is four times higher than that obtained by the MILD approach (≈14%). This can be ascribed to the higher etching efficiency of this approach as shown by SEM characterization. It is important to consider higher concentrations of Li-ions offered by the EN-MILD approach (Fig. S1†). This led to higher delamination yield of MXene single layer. The decrease in synthesis yield for 30 h MXene was due to MXene loss during the washing steps. Unlike previous methods that require high probe sonication times to acquire high yield of single layer MXenes,20,33,37 in our method, the 60% yield was obtained only after 10 min bath-sonication. This high yield was achieved in addition to a high colloidal concentration that is superior to the data reported in the literature (Table S5†).13,33,37 Higher synthesis of single layer MXenes with high colloidal concentration can expand MXene applications.

To further study the effect of synthesis conditions on the flake quality and size, atomic force microscopy (AFM), SEM, and scanning transmission electron microscopy (STEM) were conducted. As clearly demonstrated in Fig. 2, the synthesis conditions strongly affect the MXene flake size and morphology. The size distribution of the prepared Ti₃C₂Tₓ MXene flakes was measured using AFM and is illustrated in Fig. S3.† The average Ti₃C₂Tₓ MXene flake size synthesized by the MILD approach is about 0.8 µm while the average size increased to 1.8 µm when the EN-MILD approach was used with the same etching time. The maximum/average lateral size of MXene sheets depends on the size of initial MAX crystals but can be adjusted to some extent by the etching condition as well. Plotting and comparing the delamination (synthesis) yield and the average flake size as a function of etching time show an identical trend (Fig. S4†). It is worth noting that MXene flakes synthesized by the EN-MILD approach have fewer defects and are more resistant to breakage during the sonication. This may result in larger flakes for the EN-MILD approach. Moreover, increased HF concentration in EN-MILD can boost the etching efficiency leading to etching, intercalating, and exfoliating larger MAX particles that usually remain unetched using the MILD approach. It is important to note that the etching time is also crucial to obtain bigger flake sizes. The longer the time of etching, the higher the chance to separate bigger flakes from the MAX phase particles. This is the reason
that we did not observe many large MXene flakes at 12 h etching with EN-MILD. However, the number of larger flakes substantially increased in our approach due to the synergy of higher acid concentration and time. SEM characterization confirmed AFM results i.e. larger flakes were obtained using the EN-MILD approach.

Another interesting outcome of the SEM characterization is the morphology of the flakes. In our experiment, the original MILD method produces flakes with some defects (holes and oxides) while this can be partially/completely remediated by using the EN-MILD approach. Further characterization to confirm the SEM results was performed by utilizing dark-field STEM (Fig. 2, third column). These images reveal that the synthesis condition can significantly affect the size and morphology of the flakes. Oxidation in MXenes starts at the edges of the flakes;\textsuperscript{38} thus the smaller the flake size, the more oxidation is expected. MILD Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{x} flakes are smaller, with some holes on flakes and are decorated with white particles that can be attributed to titanium dioxide. The presence of oxygen during the etching can promote the formation of the insulative titanium dioxide which adversely affects electrical properties.

In the EN-MILD approach, the number of defects in the flakes as well as titanium dioxide particles significantly decreased (Fig. S5\textsuperscript{†}). It can be concluded that the modified synthesis approach yields Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{x} flakes not only with a larger size but also with higher quality. However, longer etching time also contributed to defect formation in the MXene flakes (30 h). The defect formation at longer etching time can be related to the formation of vacancy clusters due to the etching of Ti atoms. Sang \textit{et al.}\textsuperscript{39} showed that etching Ti\textsubscript{3}C\textsubscript{2} MXenes synthesized using concentrated HF solutions introduces vacancy clusters and defects in the flakes. These clusters can turn into the pinholes through the MXene flakes. The HF concentration at 30 h can be the highest among the synthesis conditions in this work (lowest remaining volume of etching solution as indicated in Fig. S1\textsuperscript{†}). This leads to more defective MXene flakes which are prone to breakage during the process. This can be likely the reason for the lower average flake size for MXenes synthesized with EN-MILD at 30 h compared to EN-MILD 24 h.

![Fig. 2 AFM, SEM, and STEM images (first, second and third columns, respectively) of MXene flakes for (a) MILD, and EN-MILD at different etching times: (b) 12 h, (c) 18 h, (d) 24 h, and (e) 30 h. Scale bars are: AFM images: 1 µm; SEM images: 3 µm; and TEM images: 200 nm. SEM images show transparent MXene flakes on the alumina membrane. Dark field STEM images indicate the holes for the flakes synthesized without using nitrogen and at long etching time (EN-MILD 30 h).](image-url)
To further characterize this, XPS analysis was performed on the different MXene samples. From the survey spectra (Fig. S6†) and for samples etched by the EN-MILD approach, less Al was observed for longer etching times. No obvious Al peak was observed for samples after 12 h etching indicating the complete removal of Al layers. The small signal for Al in the samples is attributed to the unetched MAX phase and impurities. On the other hand, longer etching time in EN-MILD increases O content as a sign of a higher content of oxygen functional groups (Fig. S6†). It is important to note that MXene synthesized by the MILD approach have a comparable Al content to MXene samples synthesized by the EN-MILD approach in 12 h and 18 h. Another interesting result is the amount of F content in the traditional MILD approach and EN-MILD approach here. At the same etching time, less fluorine was detected for the EN-MILD approach which can be beneficial for electrochemical properties. Considering the results from XRD and XPS patterns as well as flake size and morphology characterization, MXenes obtained after 12 h etching (with EN-MILD approach) share similar characteristics to MXenes synthesized by the MILD approach after 24 h.

To obtain a deeper understanding of the effect of modification on the chemical structure of MXenes, we analyze the high-resolution XPS core levels for Ti 2p, O 1s, and C 1s. The details of peak fitting can be found in Tables S7–S9.† It should be pointed out that all XPS characterization studies were performed without sputtering to study the chemical composition of the as-synthesized MXene surface.40,41 The high-resolution Ti 2p peaks can be deconvoluted to five sets of doublets corresponding to Ti–C, Ti$^{2+}$, Ti$^{3+}$, TiO$_2$, and Ti–F, at 454.7 eV (459.1, 455.4 eV (460.9), 456.2 eV (461.9), 457.4 eV (462.8), and 458.3 eV (463.6), respectively.40,42,43 As clearly illustrated in Table S7,† the content of TiO$_2$ is decreased in EN-MILD samples which is in agreement with TEM observation where fewer TiO$_2$ particles were decorated on the MXene flake edges using the EN-MILD approach. These two observations confirm that the EN-MILD approach minimizes the TiO$_2$ amount, and thus gives rise to higher electrical conductivity and better electrochemical performance.44–47 As shown in the XPS fitting details of Ti 2p, the surface of all samples was terminated by O- and F-containing functional groups. A drastic change was noticed when the MAX phase was etched at 24 h by the EN-MILD approach (see the high-resolution O 1s regions in Fig. 3b). An obvious large peak was seen at 532.5 eV confirming the OH functional group formation.40,42 The higher content of oxygen functional groups can lead to higher capacitance as will be discussed later. The high-resolution C 1s spectrum can be fitted to 5 components centered about 281.5, 284.7, 286.1, 286.7, and 288.3 which are attributed to Ti–C, C–C, C–O, HO–C=O, and C–F, respectively.42,43,48,49 The intensity of C–C peaks for the modified samples gradually increases with longer etching time. This can be attributed to more etching of Ti atoms from the structure, resulting in more exposed C.50

![Fig. 3](image-url) Component peak fitting of XPS spectra of Ti$_x$C$_2$Tx MXenes etched under different conditions: (a) Ti 2p region, (b) O 1s region, and (c) C 1s region. The high-resolution fittings indicate higher oxygen functional groups for EN-MILD samples with longer etching time. (d) Electrical conductivity of freestanding papers prepared with different MXene flakes. Employing the EN-MILD approach increased the electrical conductivity to 6 times higher than that MILD approach; cross-sections of MXene films prepared by (e) MILD approach and (f) EN-MILD after 24 h etching, respectively. The scale bar is 3 µm.
The difference in the chemical composition and structure of MXene flakes can cause different electrical conductivity as illustrated in Fig. 3d. It was previously reported that Ti$_3$C$_2$T$_x$ MXenes have a high affinity to water molecules. Thus, to minimize the effect of water intercalation on electrical conductivity, the measurement was performed after drying freestanding papers under vacuum for 4 h at 60 °C. Accurate measurement of the film thickness is crucial in electrical conductivity calculation. To eliminate errors in thickness measurement, all measurements were performed using a Dual-beam Focused Ion Beam (Fig. S7†). Generally, MXenes synthesized by the EN-MILD approach showed higher electrical conductivity compared to MILD MXene. The results for 18 h and 24 h MXenes (using EN-MILD) are by far higher than that any electrical conductivity reported to date for Ti$_3$C$_2$T$_x$ MXenes. Flake size, morphology, surface chemistry, and intercalated Li-ions are the main components that should be considered. AFM and SEM characterizations revealed larger flakes for MXenes produced with the EN-MILD approach at 18 h and 24 h etching time. Controlling the MXene flake size is crucial to obtain higher electrical conductivity. The mechanism behind this phenomenon is the lower inter-sheet contact resistance in a film containing larger MXene sheets as well as better alignment in the freestanding MXene film. Thus, the enhanced conductivity can be ascribed to less inter-sheet resistance and better alignment of thin films fabricated by EN-MILD 18 h and EN-MILD 24 h MXenes. On the other hand, MXenes synthesized by the MILD approach have some hole defects which can decrease electrical conductivity. There were significantly less holes on MXene flakes using the EN-MILD approach. Longer etching time (30 h) led to defect formation, which results in lower electrical conductivity. In addition, the lower degree of oxidation (TiO$_2$ content as shown in TEM images in Fig. 2) for the modified samples provides higher electrical conductivity. The ICP-MS measurements demonstrated that the amount of Li ions in the MXene freestanding papers decreased by using the EN-MILD approach (Li : Ti ratio was 0.018 and 0.003 for MILD and EN-MILD 24 h-MXene, respectively). Less intercalated Li-ions in combination with the decrease of stabilization of intercalated H$_2$O improved the electrical conductivity. To further examine the effect of gradually increasing the acid and Li-ion concentrations through the etching (EN-MILD approach) on electrical conductivity, we did an experiment with a higher HCl concentration and more LiF to possibly create a concentrated etchant (Table S3†). Lower electrical conductivity was obtained which demonstrates the advantages of the proposed EN-MILD approach here. This finding suggests better performance for MXene devices where larger electrical conductivity is required, i.e. applications such as electromagnetic interference shielding, wearable electronics, and wireless communications.

The electrochemical capacitive performances of the MXene samples are evaluated using a three electrode Swagelok cell. The cyclic voltammetry (CV) curves at a scan rate of 2 mV s$^{-1}$ for different MXene electrodes are shown in Fig. 4a (the CV curves with different scan rates are shown in Fig. S8†). The CV curves of all electrodes show a similar single pair of redox peaks, which indicates that the capacitance is mainly pseudocapacitance, associated with reversible intercalation/de-intercalation of protons along with the change of Ti oxidation. When the etching time is higher than 12 h in the EN-MILD approach, MXenes show higher specific capacitance (larger integral area), and EN-MILD 24 h-MXene has the highest capacitance. However, the hysteresis between the anodic and cathodic scans shows that the EN-MILD MXene electrodes have more sluggish reversibility.

![Fig. 4](image-url) Capacitive performances of the synthesized MXene in 3.0 M H$_2$SO$_4$ electrolyte: (a) cyclic voltammetry curves at a scan rate of 2 mV s$^{-1}$; (b and c) galvanostatic charge–discharge performance of Ti$_3$C$_2$T$_x$–MILD and Ti$_3$C$_2$T$_x$–EN-MILD 24 h electrodes, respectively; (d and e) gravimetric (F g$^{-1}$) and volumetric (F cm$^{-3}$) capacitances at different specific currents for the synthesized MXene; (f) capacitance retention test of an EN-MILD 24 h MXene film performed by galvanostatic cycling at 20 A g$^{-1}$. The inset shows the voltage profile for representative cycles. The synthesized MXene demonstrates excellent cycle performance, keeping 98.8% of its initial capacitance after 10 000 cycles.
The kinetic analysis based on the power law also shows slightly more diffusion-controlled kinetics for EN-MILD synthesized MXene electrodes compared to the MXene electrodes synthesized with the MILD approach (Fig. S9†). The sluggish kinetics might be caused by the larger flake size of the EN-MILD synthesized MXene, which increases the ion diffusion path within the electrode.56

Fig. 4b and c represent the galvanostatic charge/discharge curves between −0.6 and 0.2 V (vs. Ag/AgCl) at different current densities for MXene electrodes prepared by the MILD approach and EN-MILD approach and etched for 24 h, respectively (more results can be found in Fig. S10†). It can be found that these charge/discharge curves are nonlinear and deviate from the triangular shape, the typical characteristic of electric double-layer capacitors, indicating the pseudocapacitive nature of MXene electrodes. As is shown, at the same current density, EN-MILD 24 h-MXene needs much longer charging and discharging time to reach the cutting off voltage, which corresponds to higher specific capacitance. The gravimetric and volumetric capacitances for all MXene electrodes in this study at different current densities are shown in Fig. 4d and e, respectively. Among these electrodes, the EN-MILD 24 h-MXene electrode exhibits the highest specific capacitance of ≈490 F g⁻¹ at a current density of 1 A g⁻¹, significantly higher than that of MILD-MXene (324 F g⁻¹ at 1 A g⁻¹). The specific capacitance for all synthesized MXene electrodes decreases along with the increase of current density. Moreover, all the electrodes made by the EN-MILD approach and etched for more than 12 h have higher specific capacitance compared to MILD-MXene, which is consistent with the CV study. The cyclability of the EN-MILD 24 h-MXene is shown in Fig. 4f, 98.8% of capacity retained after 10 000 cycles at 20 A g⁻¹, which shows the good stability of the electrode.

The capacitance change along with the conductivity for different MXene electrodes is shown in Fig. S11; the capacitance of the MXene electrodes increases with an increase in the conductivity, except for the EN-MILD 12 h-MXene electrode, which shows smaller capacitance than the one made by the MILD approach. Since the structure of the EN-MILD 12 h-MXene electrode does not show obvious difference compared to MILD-MXene electrode (Fig. 2), we think the main reason for the lower capacitance is the different surface chemistry. Specifically, a lower amount of oxygen functional groups compared to MILD MXenes could cause lower capacitance for the EN-MILD 12 h-MXene electrode.54,55 For the MXene electrodes prepared by the MILD approach, the specific capacitance increases from 295 F g⁻¹ for 12 h-MXene (8.0 × 10⁴ S cm⁻¹) to 490 F g⁻¹ for the 24 h-MXene (2.4 × 10⁴ S cm⁻¹), then decreases to 400 F g⁻¹ for the 30 h-MXene electrode (8.5 × 10³ S cm⁻¹). These results clearly show the correspondence between the capacitance and the conductivity, which proves the direct impact of the electrical conductivity on the capacitance for MXene based supercapacitor electrodes.

In addition to the effect of the conductivity, we think that the surface chemistry has also a significant effect on the capacitive response of MXenes in acidic electrolytes. A decreased amount of fluorine functional groups relative to those of O and OH, and increased specific capacitance will negatively affect proton reduction.11,54,55,57,58 On the other hand, the higher amount of oxygen functional groups which involve in bonding/debonding transformation results in higher capacitance.11,55,58,59 The XPS analysis revealed that the EN-MILD approach induced more oxygen functional groups and less F + Cl content at the surface of MXene, especially for EN-MILD 24 h MXene (F + Cl : Ti ratio decreased from 0.52 to 0.38 for MILD and EN-MILD 24 h-MXene, respectively; Fig. S6 and Table S6†). So, the ultra-high capacitance for the EN-MILD 24 h-MXene can be due to a combined contribution of conductivity and surface chemistry.

3. Conclusion

In summary, the EN-MILD synthesis approach introduced here significantly improved the electrical conductivity of Ti₃C₂Tₓ MXenes as high as 2.4 × 10⁴ S cm⁻¹, which is the highest among values reported in the literature for this MXene. This significant improvement in electrical conductivity was attributed to a higher flake size and better quality of MXene flakes synthesized by our EN-MILD approach. Furthermore, the EN-MILD approach enhanced the synthesis aspects such as synthesis yield (up to ≈60%) and MXene colloidal concentration (up to 31 mg ml⁻¹), which can be beneficial for applications that need high colloidal concentration. The prepared MXene was used as a working electrode in a supercapacitor and demonstrated a promising capacitance of ≈490 F g⁻¹ at 1 A g⁻¹.

Conflicts of interest

The authors declare no conflicts of interest.

Acknowledgements

We would like to thank the Natural Sciences and Engineering Research Council of Canada and Killam Laureates for financial support. Material characterization was carried out in part in the Materials Research Laboratory Central Facilities, University of Illinois. Special thanks to Dr J. Kohanek for designing the schematics in Fig. 1. The authors are grateful to Dr K. Liang for useful discussions.

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