Characterization of hybrid Ti$_3$C$_2$T$_x$/PANI electrodes with different PANI contents

In order to understand the effect of the amount of deposited PANI on the performance of electrodes, hybrid Ti$_3$C$_2$T$_x$/PANI flakes were prepared using different Ti$_3$C$_2$T$_x$ to aniline ratios in the synthesis process. **Fig. S1** shows the XRD patterns of the films prepared using MXene to aniline weight ratios of 1:2, 1:4, and 1:500. As the ratio of aniline increases, the (0002) peak of MXene in the fabricated freestanding film shifts to lower angles which is an indication of increased interlayer spacing of Ti$_3$C$_2$T$_x$ flakes. For a film prepared by a precursor solution with very high aniline content (1:500 sample), the (0002) peak shifted down to 4.7º corresponding to a $c$-lattice parameter ($c$-LP) of 37.8 Å.

**Fig S2** shows the FTIR spectrum of the 1:500 sample. Compared to the samples prepared using low amounts of aniline, in this sample the corresponding peaks for PANI are intensified. This is due to the increased amount of PANI in final hybrid film which is in good agreement with the large interlayer spacing observed for this sample in the XRD experiments.
Figure S2. FTIR spectrum of Ti$_3$C$_2$Tx/PANI hybrid films prepared using MXene to aniline ratio of 1:500. The peak at 1566 cm$^{-1}$ corresponds to C=C stretching vibrations of quinonoid ring and the peaks at 1366 cm$^{-1}$ and 1217 cm$^{-1}$ correspond to C-N stretching vibrations. The peak at 1164 cm$^{-1}$ can be assigned to C-H stretching of aromatic amine. Also, the transmittance peaks observed at 106 cm$^{-1}$ and 802 cm$^{-1}$ correspond to C-H out-of-plane vibration of the benzene ring.

Figure S1. XRD patterns of the hybrid Ti$_3$C$_2$Tx/PANI films prepared using different MXene to aniline ratios of 1:2, 1:4, and 1:500. By increasing the aniline to MXene ratio, the (0002) peak slowly shifts to lower angles and for very high ratio of 1:500 the intensity of MXene peaks decrease due to loss of ordering in the MXene/PANI films.
Figure S3. Atomic force microscopy (AFM) images and corresponding height profiles of (a) as synthesized Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{x}, (b) and (c) Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{x}/PANI hybrids (with 1:2 MXene to aniline ratio) prepared in this study. The formation of island shape PANI chains on MXene flakes can be seen in these images. Thickness of single layer flakes of Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{x} is \~2.7 nm. However, after polymerization of aniline on surface of MXene, the functionalized Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{x} sheets are crumpled and their thicknesses increases to about \~6 nm.
As it is shown in Figure S5a, by increasing the ratio of aniline monomer in the synthesis process beyond 1:2 (MXene to aniline), the electrochemical performance of the MXene/PANI hybrid electrodes decreases. As we have explained in the paper, the deposited PANI on MXene sheets does not directly contribute to the charge storage in the fabricated electrode as it is not...
electrochemically active in the potential window that Ti$_3$C$_2$Tx is active in sulfuric acid electrolytes. PANI only acts as a conductive spacer between the MXene layers. Therefore, the presence of excessive amounts of PANI in the hybrid electrodes’ structure will increase the inactive component (deadweight) of the electrodes and reduces the specific capacitance of the hybrid material. This explains why the capacitance of the electrode with MXene to aniline ratios of 1:5 and 1:10 is lower than the electrodes with a ratio of 1:2.

Table S1. EDS results showing atomic percentage of different elements present in the pristine Ti$_3$C$_2$Tx and Ti$_3$C$_2$Tx/PANI hybrids for a sample prepared with high loading of aniline monomer.

<table>
<thead>
<tr>
<th></th>
<th>Ti</th>
<th>O</th>
<th>Cl</th>
<th>F</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>As prepared</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MXene</td>
<td>23.69%</td>
<td>24.59%</td>
<td>2.18%</td>
<td>10.22%</td>
<td>0%</td>
</tr>
<tr>
<td>After PANI</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>deposition</td>
<td>9.88%</td>
<td>15.71%</td>
<td>0.89%</td>
<td>4.13%</td>
<td>33.3%</td>
</tr>
</tbody>
</table>
Figure S6. Capacitive charge storage contribution for a 3.5 µm thick Ti3C2Tx electrode at scan rate of (a) 2 mV s⁻¹ and (b) 20 mV s⁻¹, for a 4 µm thick Ti3C2Tx/PANI hybrid electrode at scan rate of (c) 2 mV s⁻¹ and (d) 20 mV s⁻¹, and for a 10 µm thick Ti3C2Tx film at scan rate of (e) 2 mV s⁻¹ and (f) 20 mV s⁻¹.
Figure S7. Comparison of CVs of MXene and MXene/PANI hybrid electrodes reported in this study at scan rates of (a) 2 mV s$^{-1}$ and (b) 100 mV s$^{-1}$.

Figure S8. CV curves of (a) a 3.5 µm thick Ti$_3$C$_2$Tx electrode, (b) a 10 µm thick Ti$_3$C$_2$Tx electrode, (c) a 9 µm thick Ti$_3$C$_2$Tx crumpled with HCl, (d) a 13 µm thick Ti$_3$C$_2$Tx/PANI hybrid electrode, (e) a 20 µm thick Ti$_3$C$_2$Tx/PANI hybrid electrode, and (f) a 45 µm thick Ti$_3$C$_2$Tx/PANI electrode at scan rates ranging from 5 mV s$^{-1}$ to 1 V s$^{-1}$. 
Figure S9. Thermogravimetric analysis (TGA) data of a pristine Ti$_3$C$_2$T$_x$ films, a hybrid film prepared using the Ti$_3$C$_2$T$_x$ to aniline ratio of 1:2, a hybrid film prepared using the Ti$_3$C$_2$T$_x$ to aniline ratio of 1:500, and pure PANI. The TGA experiments were carried out under O$_2$ atmosphere.

Figure S10. A symmetric supercapacitor prepared with two Ti$_3$C$_2$T$_x$/PANI hybrid electrodes (4 µm thickness) in 3M H$_2$SO$_4$. (a) CVs at various scan rates ranging from 2 mV s$^{-1}$ to 100 mV s$^{-1}$ in a 1V voltage window and (b) Corresponding gravimetric and volumetric capacitances of the cell at different scan rates.
Figure S11. Ragone plots of the symmetric MXene/PANI supercapacitor with (a) gravimetric and (b) volumetric power and energy densities of the cell compared to a previously reported symmetric supercapacitor based on MXene/graphene hybrid electrodes.1 (reference 1 in this document /reference 25 in the paper) The energy and power densities are calculated by considering the total mass of the active material in the symmetric cell.

References