

## Supplementary Information

# Interlayer pillaring influences the octahedral tilting and electrochemical capacitance of tungsten oxides

Ran Ding, Michael A. Spencer, Noah P. Holzapfel, Matthew Chagnot, and Veronica Augustyn\*

Department of Materials Science and Engineering

North Carolina State University, Raleigh, NC USA 27695

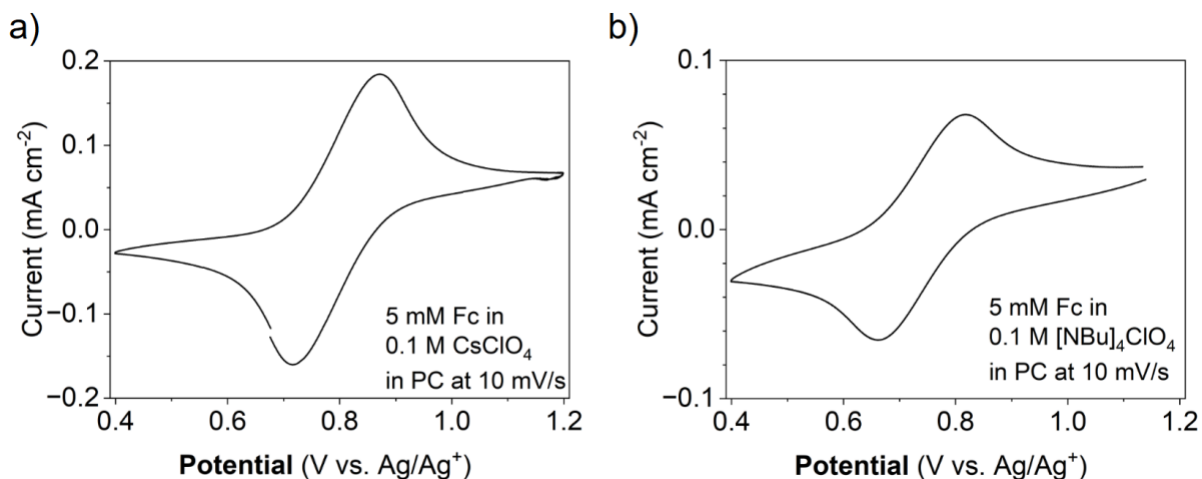
\* Corresponding author: [vaugust@ncsu.edu](mailto:vaugust@ncsu.edu)

## Table of Contents

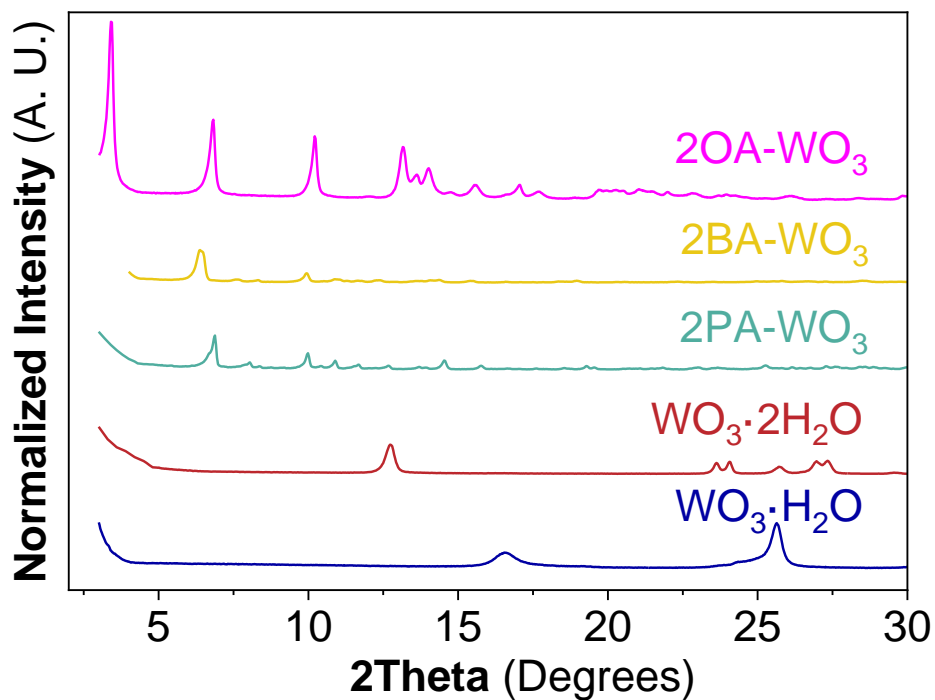
<b>Table S1.</b> Observed Raman peaks and assignment of $\text{WO}_3 \cdot 2\text{H}_2\text{O}$ and BA-pillared .....	<b>S2</b>
<b>Figure S1.</b> CV of 5 mM ferrocene (Fc) dissolved in (a) 0.1 M $\text{CsClO}_4$ or (b) 0.1 M $[\text{NBu}]_4\text{ClO}_4$ in PC used to calibrate the potential vs. SHE. ....	<b>S3</b>
<b>Figure S2.</b> XRD of pillared $\text{WO}_3$ with different alkyl chain lengths and saturated interlayers ....	<b>S3</b>
<b>Figure S3.</b> Different colors of BA- $\text{WO}_3$ due to different ratios of butylamine to $\text{WO}_3 \cdot 2\text{H}_2\text{O}$ during synthesis. ....	<b>S4</b>
<b>Figure S4.</b> XRD of octylamine pillared $\text{WO}_3$ with various ratios between OA and $\text{WO}_3$ .....	<b>S4</b>
<b>Figure S5.</b> TGA curves for $\text{WO}_3 \cdot \text{H}_2\text{O}$ , $\text{WO}_3 \cdot 2\text{H}_2\text{O}$ , butylammonium pillared tungsten oxides 0.5BA- $\text{WO}_3$ , 1BA- $\text{WO}_3$ and 2BA- $\text{WO}_3$ , and octylammonium pillared tungsten oxides 2OA- $\text{WO}_3$ . Atmosphere: air; heating rate: $2^\circ\text{C}/\text{min}$ .....	<b>S5</b>
<b>Figure S6.</b> CVs of $\text{WO}_3 \cdot n\text{H}_2\text{O}$ and OA- $\text{WO}_3$ with various ratios between OA and $\text{WO}_3$ in the solution of 0.1M $\text{LiClO}_4$ . WE: slurry of tungstates on carbon paper; CE: Pt coil; RE: Li metal; scan rate: 1mV/s. ....	<b>S5</b>
<b>Figure S7.</b> Raman of fully butylammonium pillared tungsten oxides 2BA- $\text{WO}_3$ in 1 M $\text{H}_2\text{SO}_4$ after 250 cycles .....	<b>S6</b>
<b>Figure S8.</b> Comparison among CVs of OA- $\text{WO}_3$ with various ratios between OA and $\text{WO}_3$ in the solution of (a) 0.1M $\text{LiClO}_4$ , (b) 0.1M $\text{CsClO}_4$ and (c) 0.1M $[\text{NBu}]_4\text{ClO}_4$ .....	<b>S7</b>
<b>Figure S9.</b> The capacity of $\text{WO}_3 \cdot n\text{H}_2\text{O}$ and 0.5OA- $\text{WO}_3$ , 1OA- $\text{WO}_3$ and 2OA- $\text{WO}_3$ in different electrolytes.....	<b>S8</b>
<b>Figure S10.</b> Ex situ Raman spectroscopy of a 0.5BA- $\text{WO}_3$ electrode before and after electrochemical reduction in 0.1 M $\text{LiClO}_4$ in PC to 2 V vs. $\text{Li}/\text{Li}^+$ .....	<b>S8</b>
<b>Figure S11.</b> Ex situ XRD of a 0.5BA- $\text{WO}_3$ electrode before and after electrochemical reduction in 0.1 M $\text{LiClO}_4$ in PC to 2 V vs. $\text{Li}/\text{Li}^+$ .....	<b>S9</b>
<b>Figure S12.</b> In situ XRD of 0.5BA- $\text{WO}_3$ in 0.1 M $\text{LiClO}_4$ in PC.....	<b>S9</b>

**Table S1.** Observed Raman peaks and assignments for  $\text{WO}_3 \cdot 2\text{H}_2\text{O}$  and  $\text{BA-WO}_3$ .

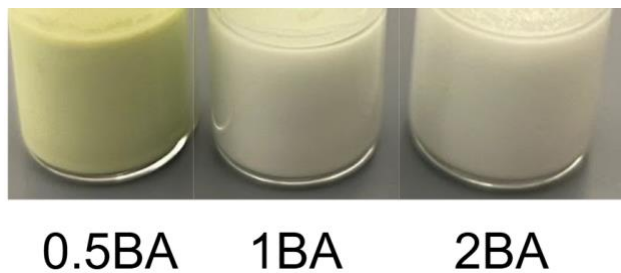
Frequency ( $\text{cm}^{-1}$ )	$\text{WO}_3$	$\text{BA-WO}_3$
2800-2900	--	$\nu(\text{C-H})$
1470	--	$\delta(\text{CH}_2)$
950	$\nu(\text{W-O}_t)$	$\nu(\text{W-O}_t)$
860, 890	--	$\nu(\text{W-O}_t)$
600-700	$\nu(\text{O-W-O})$	--
330	$\delta(\text{O-W-O})$	$\delta(\text{O-W-O})$
210	lattice mode	lattice mode



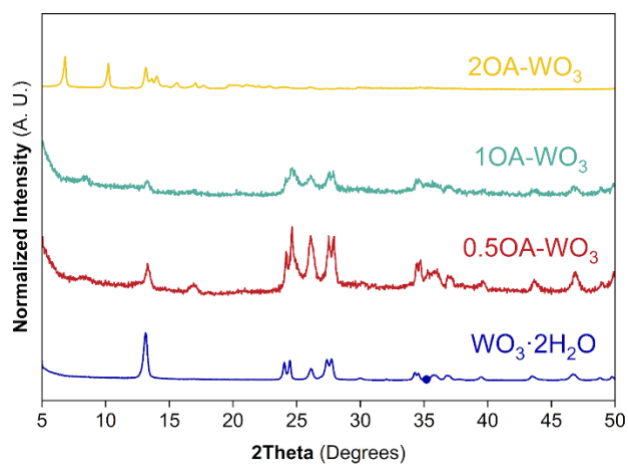
**Figure S1.** CV at 10 mV/s for 5 mM ferrocene (Fc) dissolved in (a) 0.1 M CsClO<sub>4</sub> in PC or (b) 0.1 M [NBu<sub>4</sub>]<sub>4</sub>ClO<sub>4</sub> in PC.



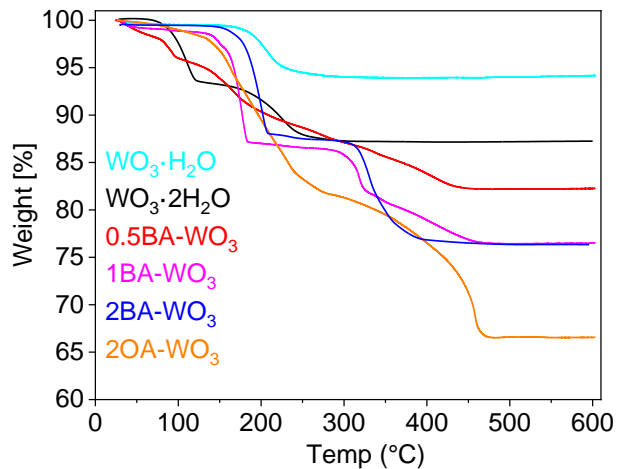
**Figure S2.** XRD of hydrated WO<sub>3</sub> and alkylammonium-cation pillared WO<sub>3</sub> with different alkyl chain lengths.



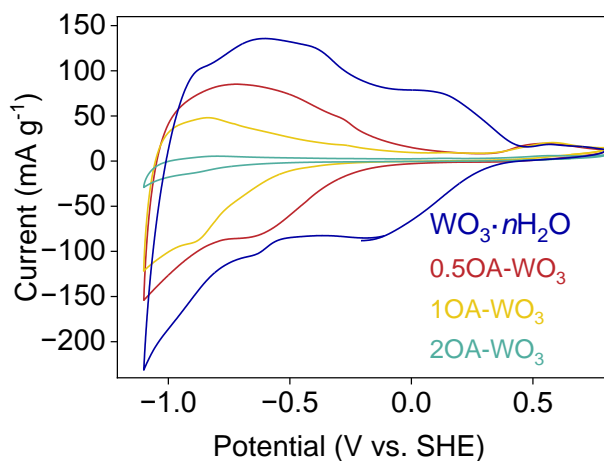
**Figure S3.** Different colors of BA-WO<sub>3</sub> due to different ratios of butylamine to WO<sub>3</sub>·2H<sub>2</sub>O during synthesis.



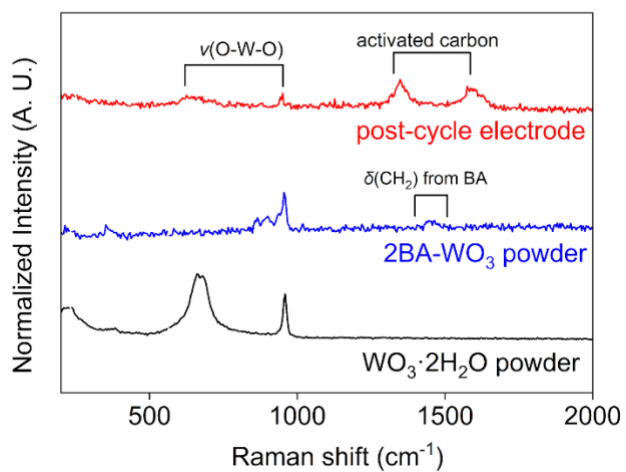
**Figure S4.** XRD of OA-WO<sub>3</sub> with various ratios between OA and WO<sub>3</sub>.



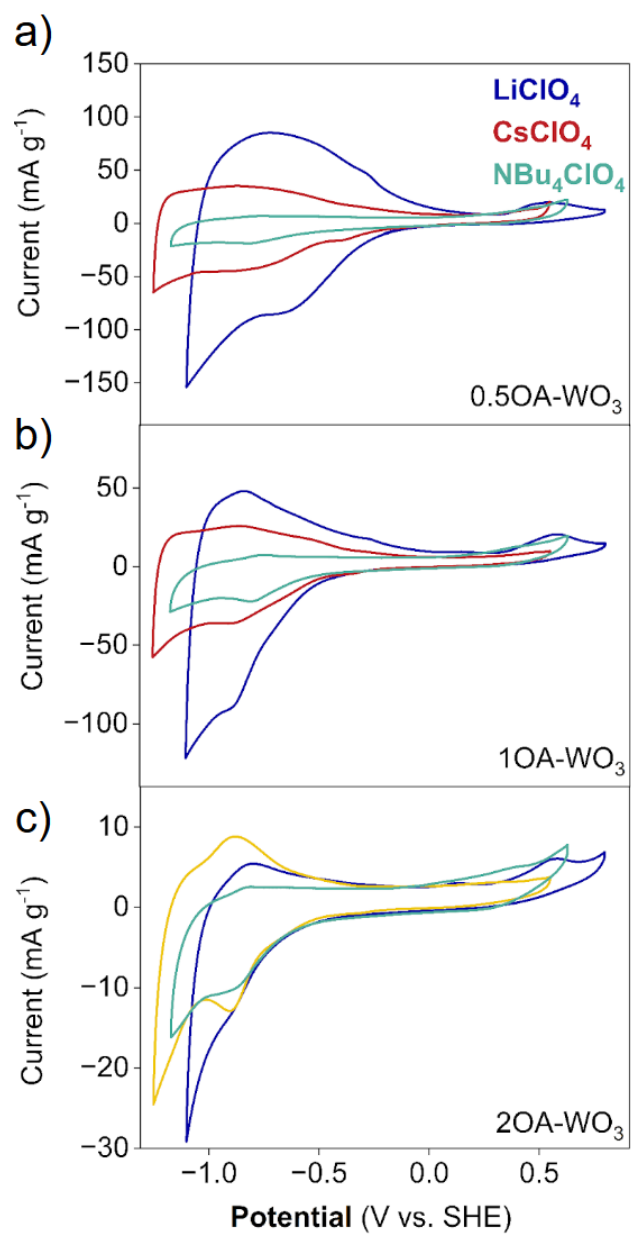
**Figure S5.** TGA curves for tungsten oxides hydrates ( $\text{WO}_3 \cdot \text{H}_2\text{O}$ ,  $\text{WO}_3 \cdot 2\text{H}_2\text{O}$ ), BA pillared tungsten oxides ( $0.5\text{BA-WO}_3$ ,  $1\text{BA-WO}_3$ , and  $2\text{BA-WO}_3$ ), and OA pillared tungsten oxides ( $2\text{OA-WO}_3$ ). TGA measurements were performed in air with a heating rate of  $2^\circ\text{C}/\text{min}$ .



**Figure S6.** CVs at  $1 \text{ mV}/\text{s}$  of  $\text{WO}_3 \cdot n\text{H}_2\text{O}$  and  $\text{OA-WO}_3$  with various ratios between OA and  $\text{WO}_3$  in  $0.1 \text{ M LiClO}_4$  in PC.

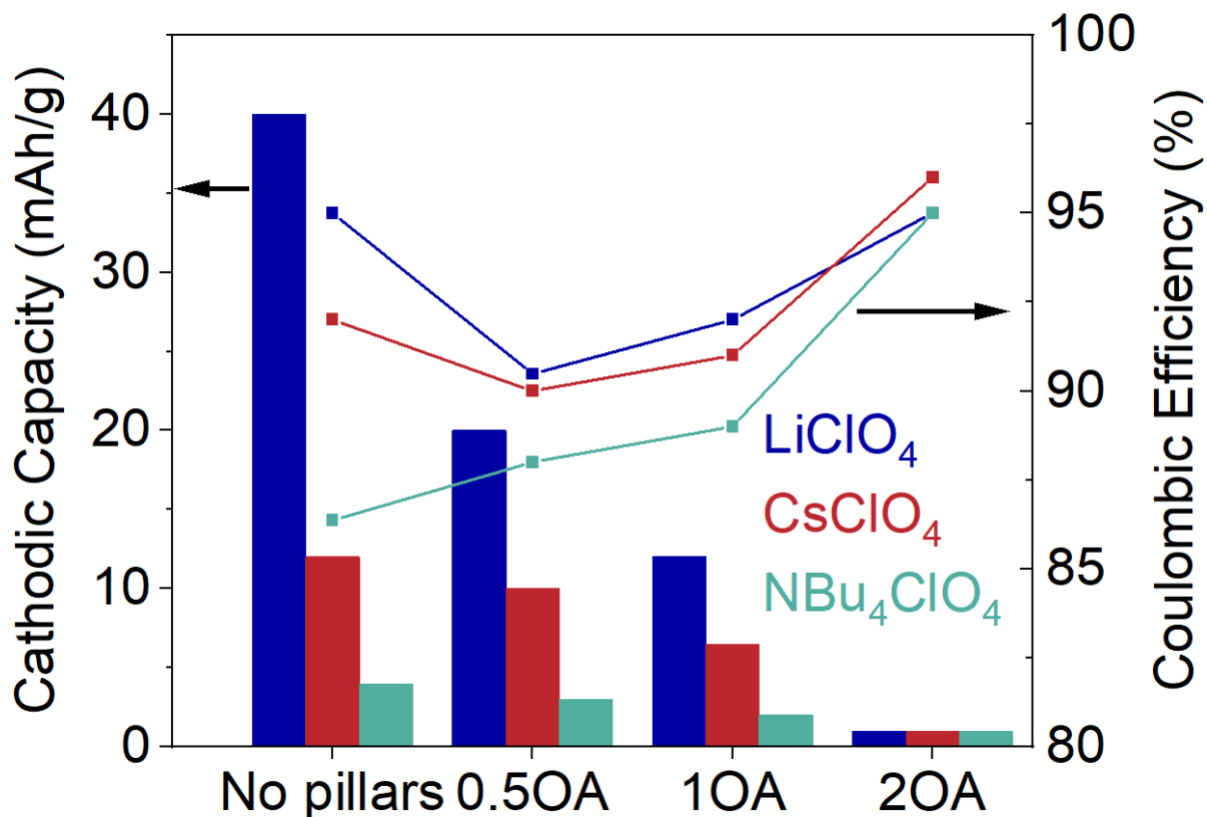


**Figure S7.** Ex situ Raman spectroscopy of an electrode consisting of fully BA-pillared tungsten oxide, 2BA-WO<sub>3</sub>, after 250 cycles at 10 mV/s in 1 M H<sub>2</sub>SO<sub>4</sub> and comparison to as-synthesized 2BA-WO<sub>3</sub> and WO<sub>3</sub>·2H<sub>2</sub>O powders.

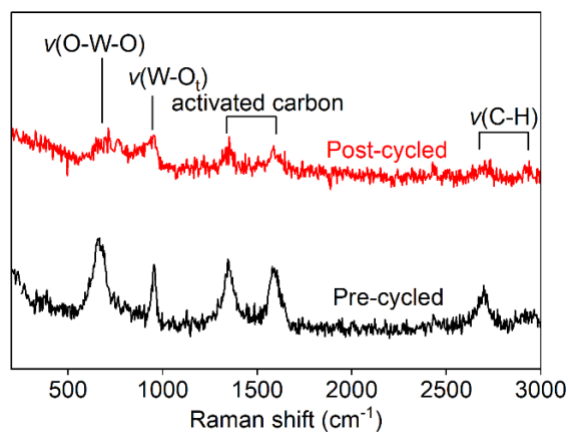


**Figure S8.** Comparison among CVs of OA-WO<sub>3</sub> with various ratios between OA and WO<sub>3</sub> in the solution of (a) 0.1 M LiClO<sub>4</sub>, (b) 0.1 M CsClO<sub>4</sub> and (c) 0.1 M [NBu<sub>4</sub>]<sub>4</sub>ClO<sub>4</sub> in PC

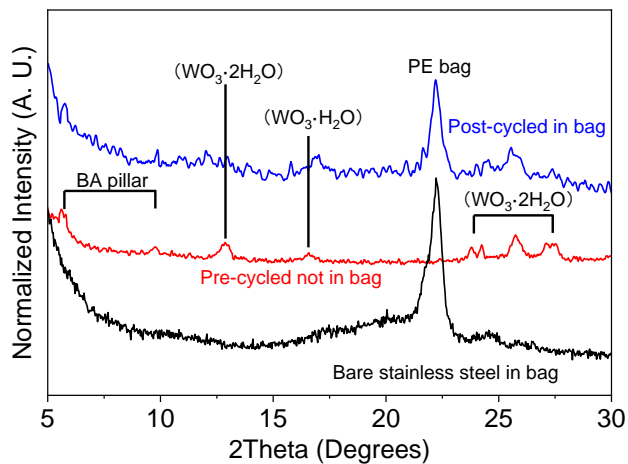




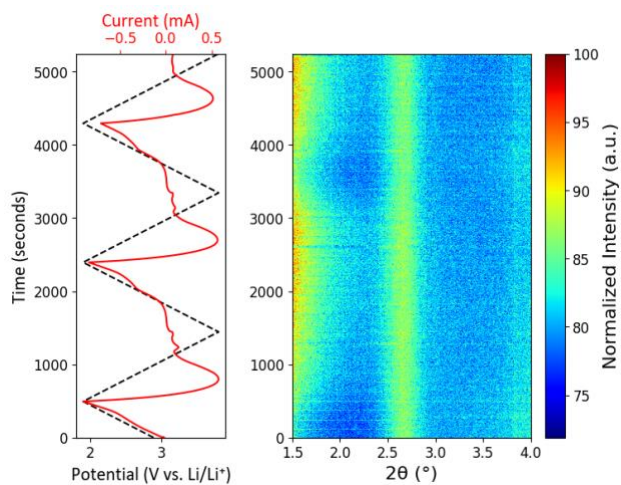
**Figure S9.** The capacity of  $\text{WO}_3 \cdot n\text{H}_2\text{O}$  and  $0.5\text{OA-WO}_3$ ,  $1\text{OA-WO}_3$  and  $2\text{OA-WO}_3$  in different electrolytes. The bar graph is for cathodic capacity in left  $y$ -axis and scatter/line graph is for coulombic efficiency in right  $y$ -axis.



**Figure S10.** Ex situ Raman spectroscopy of a  $0.5\text{BA-WO}_3$  electrode before and after electrochemical reduction in  $0.1 \text{ M LiClO}_4$  in PC to  $2 \text{ V vs. Li/Li}^+$ .



**Figure S11.** Ex situ XRD of 0.5BA- $\text{WO}_3$  before and after electrochemical reduction in 0.1 M  $\text{LiClO}_4$  in PC to 2 V vs.  $\text{Li/Li}^+$ .



**Figure S12.** In situ electrochemical XRD of 0.5BA- $\text{WO}_3$  coated on stainless steel (SS) mesh in 0.1 M  $\text{LiClO}_4$  in PC. Cyclic voltammetry was performed between 2 – 3.9 V at a scan rate of 2 mV/s.