

# Novel CNT Supported Molybdenum Catalyst for Detection of L-Cysteine in Its Natural Environment

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## S1. Materials

Mo(II)Chloride (  $\text{MoCl}_2$  99.99 %  $\geq$  ), L-C ( 99.99  $\geq$  % ) sodium borohydride (  $\text{Na}[\text{BH}_4]$ , 99 % ), multi-walled carbon nanotube ( MWCNT, 98 % ) from Sigma-Aldrich and Nafion 117 solution ( 5 % ) were purchased from Aldrich. The potentiostat and the entire electrochemical system, Ag/AgCl reference electrode and Pt wire electrodes were obtained from CH Instruments. Deionized water was provided by distillation with a water purification system double distilled (Milli-Q Water Treatment System). All glass materials used in the experiments were washed with acetone and ethyl alcohol and dried in an oven.

## S2. Preparation of Nanocatalysts

Mo/CNT catalysts containing Mo metal (10% by weight) were synthesized by the  $\text{Na}[\text{BH}_4]$  chemical reduction method. To obtain the catalyst system, the Mo metal precursor was dissolved in 10 ml of deionized water for about 10 minutes and mixed with 0.1 g of CNT for 15 minutes in an ultrasound bath. It was also mixed for another 90 minutes. Sufficient  $\text{Na}[\text{BH}_4]$  was added in a molar ratio of  $\text{Na}[\text{BH}_4]$ :Mo (30:1), the metal precursor was reduced and stirred for an additional 60 minutes. The obtained metal nanocatalysts were dried in an oven at 85°C for 12 hours.

## S3. Characterization of Nanocatalyst

The Mo/CNT catalyst was made to determine physical properties SEM-EDX, XRD, and UV-Vis, TPR, TPO, TPD measurements. SEM-EDX and mapping measurements were realized utilizing a ZEISS Sigma 300 scanning electron microscope. The X-ray Diffraction (XRD) patterns were performed to examine crystal structures with an Empyrean (PANalytical) diffractometer using  $\text{Cu-K}\alpha$  ( $\lambda = 1.5406 \text{ \AA}$ ) radiation source. The UV-visible diffuse reflectance spectrum was used to analyze the surface properties of Mo/CNT catalysts. UV-VIS spectrums were recorded utilizing the Shimadzu UV-3600 Plus device.

$\text{H}_2$ -TPR,  $\text{O}_2$ -TPO, and  $\text{NH}_3$ -TPD analysis were realized with Micromeritics Chemisorb 2750 (gas-adsorption equipment) automated system attached via ChemiSoft TPx software. First of all, about 0.05 g sample was added into the quartz cell. It was then held under helium at a flow rate of 50 ml/min for about 15 min to remove moisture and impurities at 100 °C. The reactive gas compositions were 5%  $\text{H}_2/\text{Ar}$  (5 vol%  $\text{H}_2$ -95 vol% Ar) for TPR, 5%  $\text{O}_2/\text{He}$  for TPO, and 10%  $\text{NH}_3/\text{He}$  gas mixture for TPD measurements. The  $\text{H}_2$ -TPR analysis of Mo/CNT catalyst was reduced utilizing 5%  $\text{H}_2/\text{Ar}$  as the reducing gas at a heating rate of 10 °C/min up to 830 °C. TPO experiment of the catalyst was obtained with 5%  $\text{O}_2/\text{He}$  gas mixture at a heating rate of 10 °C/min up to 810 °C. The acidity and acid strength of the catalyst were defined as employing an  $\text{NH}_3$ -TPD analysis. TPD analysis was made under 10%  $\text{NH}_3/\text{He}$  gas

mixture at a heating rate of 10 °C/min from 37 °C to 300 °C. The gas flow rate was 50 mL/min at all analysis. All measurements were made on fresh samples.

#### **S4. Electrochemical Measurements**

5 mg of Mo/CNT catalyst was taken and thoroughly sonicated with 1 mL of nafion and a catalyst ink was obtained. 3 L of this catalyst ink was spread onto the GCE electrode. Cyclic voltammograms were made on Modified GCE electrodes with Mo/CNT at a scanning rate of 100 mVs<sup>-1</sup> and made with 10 mM L-C in 0.1M PBS and room temperature (25±2 °C). The effect of pH was studied via CV in PBS prepared in pH studies (5, 7.2 and 10) and 5 mM L-C. Further studies were made for the determination of L-C concentration effect through the L-C electrooxidation with CV. A scanning rate study was made at different voltages for the electrochemical activity of L-C on the Mo/CNT-modified GCE electrode. 10, 30, 50, 100, 120, 150, 180, 200, 230, 250 300, 320, 350, 380, 400. 420, 450, 480, 500 in 10 mM L-C + 0.1 M PBS (pH = 7.2) mV/sec. Differential pulse voltammetry (DPV) was also used to electrooxidation measurements for L-C at varying concentrations to identify sensitivity on Mo/CNT/GCE. Concentration calculations were made with the highest current obtained and calibration curves were drawn for DPV. Calculations were made using the slope of this calibration curve to measure the sensitivity of the sensor and the results were estimated accordingly.

EIS was taken on a Mo/CNT/GCE at different potentials at 0.1M PBS (pH 7.2) + 5mM L-C. Signal amplitude and frequency range were set to 0.02–100,000 Hz and 10 mV, respectively. CV and EIS measurements were made on Mo/CNT to study the interference. Interactions of uric acid, ascorbic acid, L-Tyrptophane, L-Tyrosine, L-C, Dopamine were investigated, potentially 1 V. Actual sample analysis measurements were measured by determining L-C in acetylcysteine effervescent tablets with DPV under the most efficient conditions. Details of these measurements were given in our previous studies [29, 30].