

Supporting Information

Preparation of zeolitic imidazolate framework and carbon nanofiber composites for nitrofurazone detection

Hao Bo Wang^{1,2}, Subramanian Sakthinathan^{1,2}, Arjunan Karthi Keyan^{1,2}, Chung Lun Yu^{1,2}, Satoshi Kameoka³, Te-Wei Chiu^{1,2*}, Karuppiyah Nagaraj⁴

Department of Materials and Mineral Resources Engineering, National Taipei University of Technology, 1, Sec. 3, Zhongxiao E. Rd., Taipei 106, Taiwan.

Institute of Materials Science and Engineering, National Taipei University of Technology, No. 1, Section 3, Chung-Hsiao East Road, Taipei 106, Taiwan.

Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Katahira 2-1-1, Sendai 980-8577, Japan.

School of Pharmacy, National Forensic Sciences University, 6M56+XP8, Police Bhavan Rd, Sector 9, Gandhinagar, Gujarat 382007, India

*Correspondence: tewei@ntut.edu.tw

S.1. Preparation of PAN/DMF precursor

First, to 0.85 g of PAN (Polyacrylonitrile, M.W. = 1,500,000 from SIGMA-ALDRICH) solute was added 7.22 mL of DMF (Dimethylformamide, from TEDIA) as the solvent, and the mixture was stirred at room temperature for 12 hr to completely dissolve the polymer and obtain a viscous gel-like precursor fluid (10 wt %) (**Figure S1**).



Figure S1. Schematic diagram of the PAN/DMF precursor preparation.

S.2. Preparation of ZIF-8 precursor

0.3085 g (approximately 1 mmol) of $\text{Zn}(\text{NO}_3)_2 \cdot 6(\text{H}_2\text{O})$ (Zinc nitrate hexahydrate, M.W. = 297.49 g/mol from SIGMA-ALDRICH) and 0.3287 g (approximately 4 mmol) of 2-methylimidazole (M.W. = 82.1 g/mol from Sigma-Aldrich) were added to 25 ml methanol at room temperature and ultrasonically stirred for 10 min, respectively.

S.3. Electrospinning setup

In a typical electrospinning setup, a high-voltage source was connected to a metallic needle, which was attached to a syringe pump. In the electrospinning process, the precursor was placed in a 10 mL syringe with a stainless steel needle. The syringe was clamped to a ring stand at the proper distance above an electrically grounded, bowl-shaped stainless steel mesh, which was used as a collector, as shown in **Figure S2**.



Figure S2 Schematic diagram of the electrospinning setup.

S.4. Electrochemical analyzer

Electrochemical studies were conducted on a CHI 1211B workstation in N_2 atmosphere and with the electrode arrangement presented in **Figure S3**. Electrochemical impedance spectroscopy (EIS) was carried out with the ZAHNER impedance analyzer (Kroanch, Germany) at frequencies of 0.1 Hz to 1 MHz. The electrochemical work system had GCE as the main working electrode, the Ag/AgCl electrode as the reference electrode, and Pt wire as the auxiliary electrode.

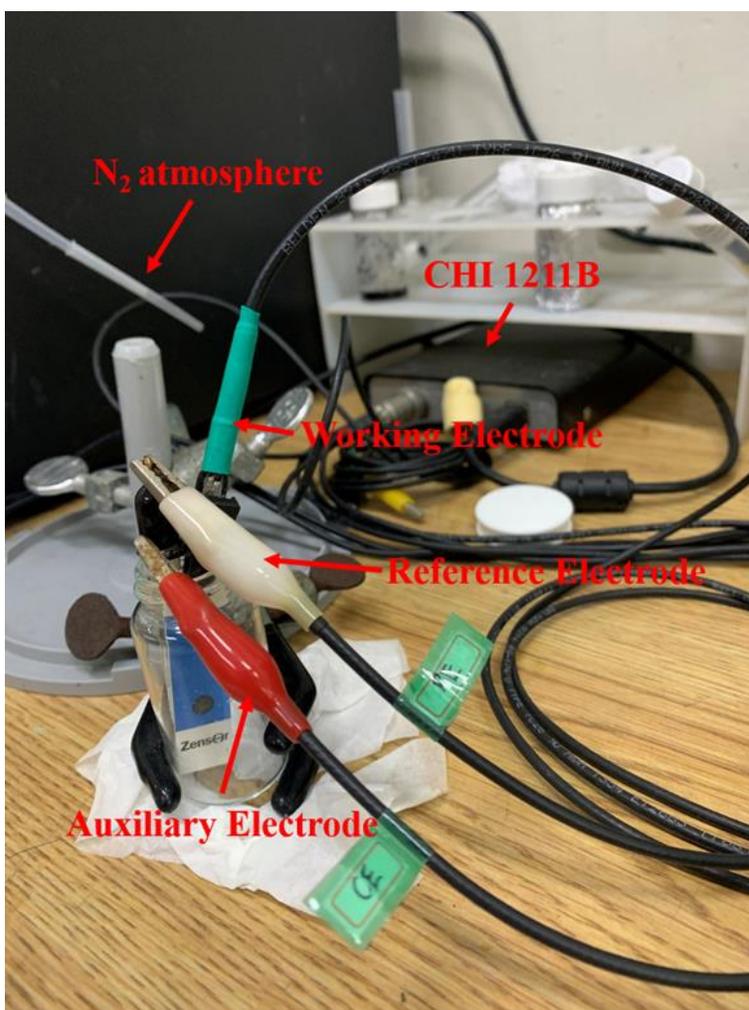


Figure S3. Photograph of electrochemical studies.

S. 5. TGA analysis of carbon nanofibers

Figure S4 shows the DSC-TGA graph of PAN nanofibers in air. It can be seen from the TG curve that there was almost no weight loss before 130 °C. When the temperature was between 130 °C and 230 °C, the DMF solvent began to volatilize at the same time PAN underwent physical shrinkage and chemical cyclization shrinkage. Therefore, nearly 5% weight loss appeared on the TG curve between 130 °C and 230 °C. After that, when the temperature rose to 230–300 °C, the fiber exhibited 10% weight loss as the fiber underwent cyclization, dehydrogenation, and oxidation reactions. The H and N elements were removed and a stable PAN molecular chain structure formed. At temperatures of 300 °C to 470 °C, the C, H, and N elements reacted with O₂ to generate gas, and the PAN fiber was completely decomposed. Therefore, we pre-oxidized the as-spun fibers at 280 °C before the carbonization. Generally, the pre-oxidation temperature should be set at about 260 °C; otherwise, the PAN fiber will be melted or even ablated.

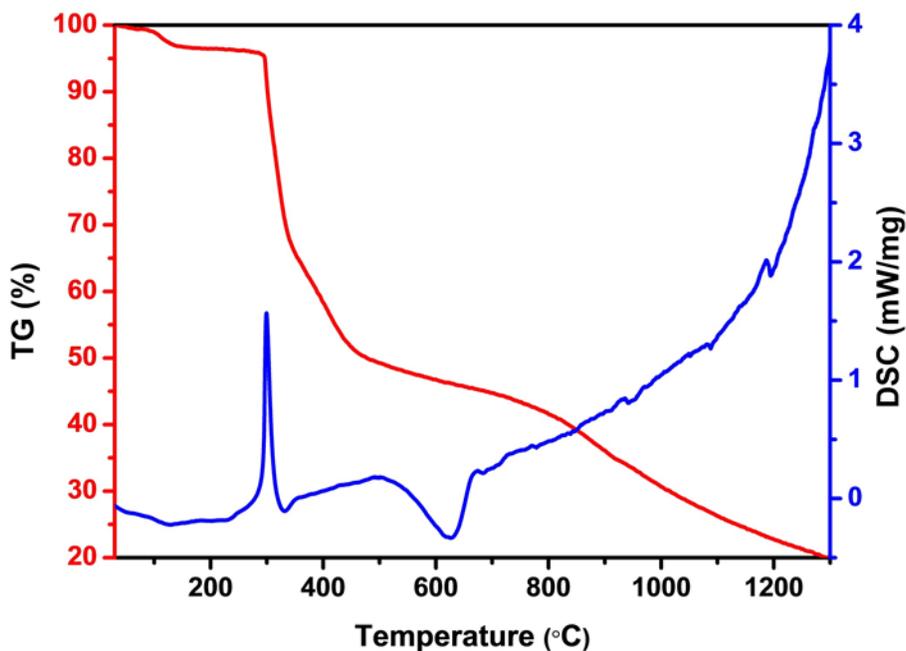


Figure S4. The DSC-TGA results for PAN nanofibers in air.

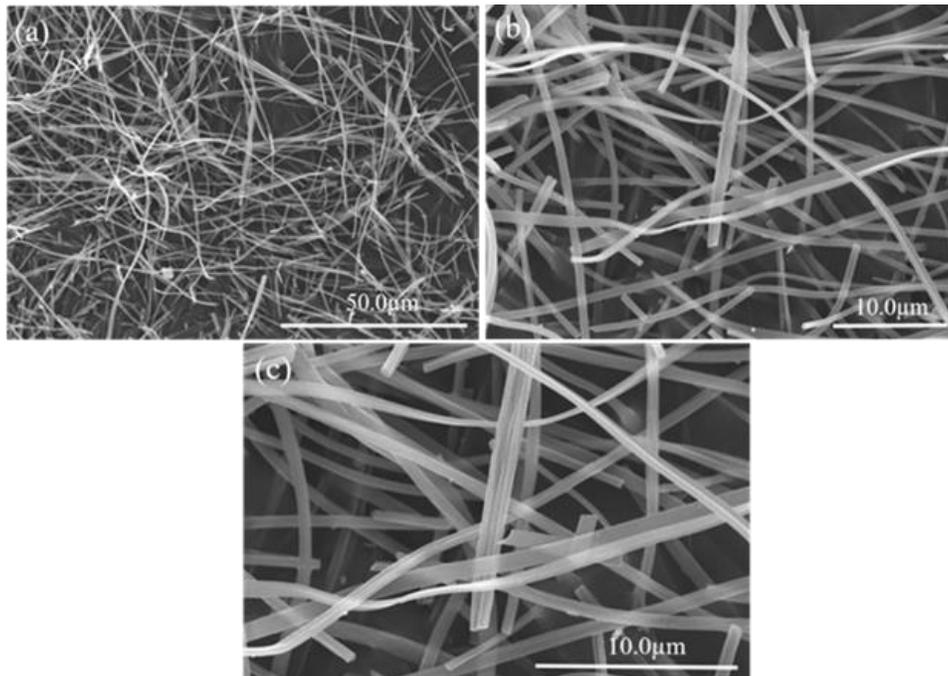


Figure S5. SEM images of 500 rpm CNFs after annealing.

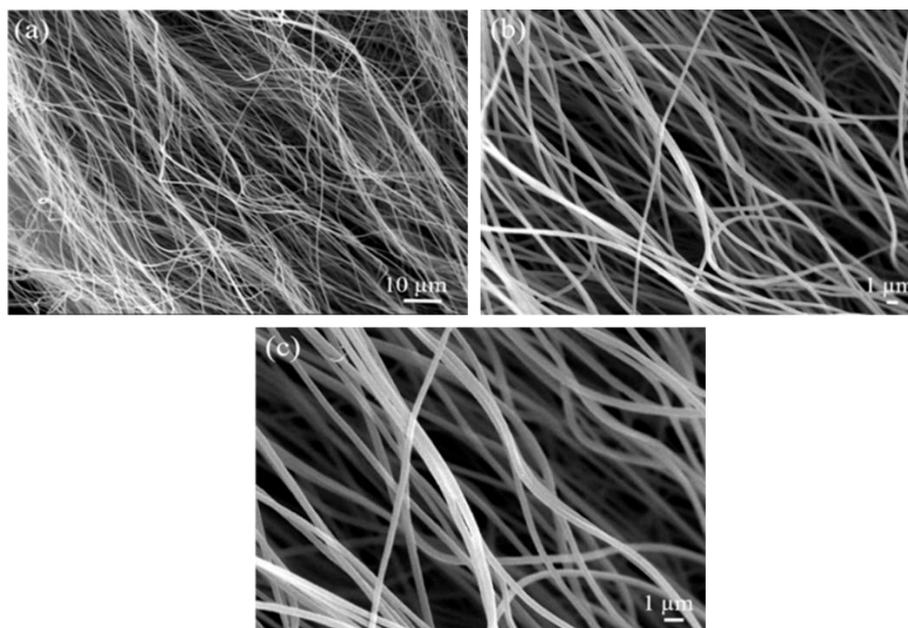


Figure S6. SEM images of 1000 rpm CNFs after annealing.

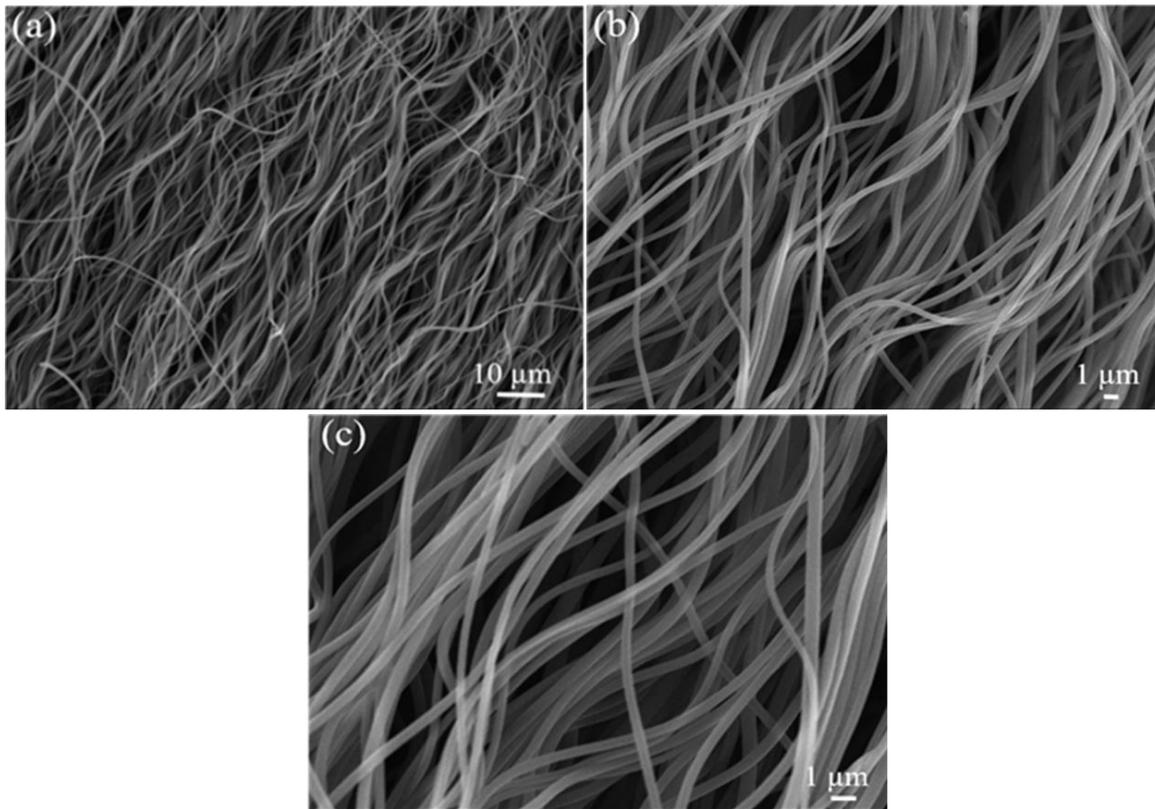


Figure S7. SEM images of 1500 rpm CNFs after annealing.

S. 6. XRD and Raman analysis of 2000 rpm CNFs

Figure S8 shows the XRD pattern of CNFs generated by an electrospinning rotating collector after annealing, and no obvious diffraction peaks are visible. Because the CNFs were an amorphous material and had undergone high-temperature annealing carbonization, they presented no obvious crystallinity.

To further study the characteristics and microstructure of 2000 rpm amorphous carbon CNFs, the graphitization degree of 2000 rpm CNFs was evaluated by Raman spectroscopy. Raman spectrum of 2000 rpm CNFs revealed that the 2000 rpm CNFs curve mainly had two strong peaks. They were the D peak at 1340 cm^{-1} and the G peak at 1576 cm^{-1} . In combination with the SEM images in Figure S8, the Raman spectroscopy clearly indicated that straight and unidirectional CNFs were successfully prepared by an electrospinning rotating collector (2000 rpm).

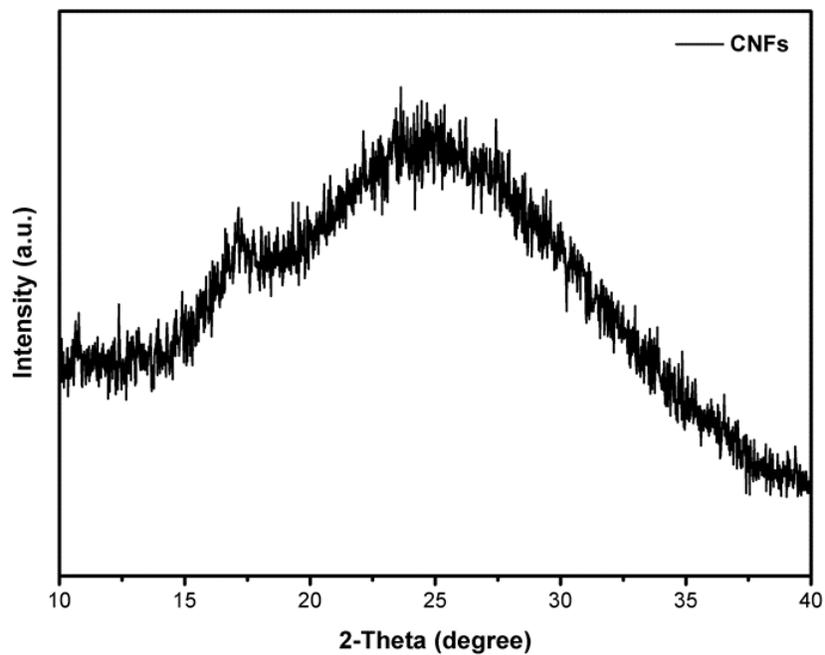


Figure S8. The XRD patterns of CNFs prepared by electrospinning.

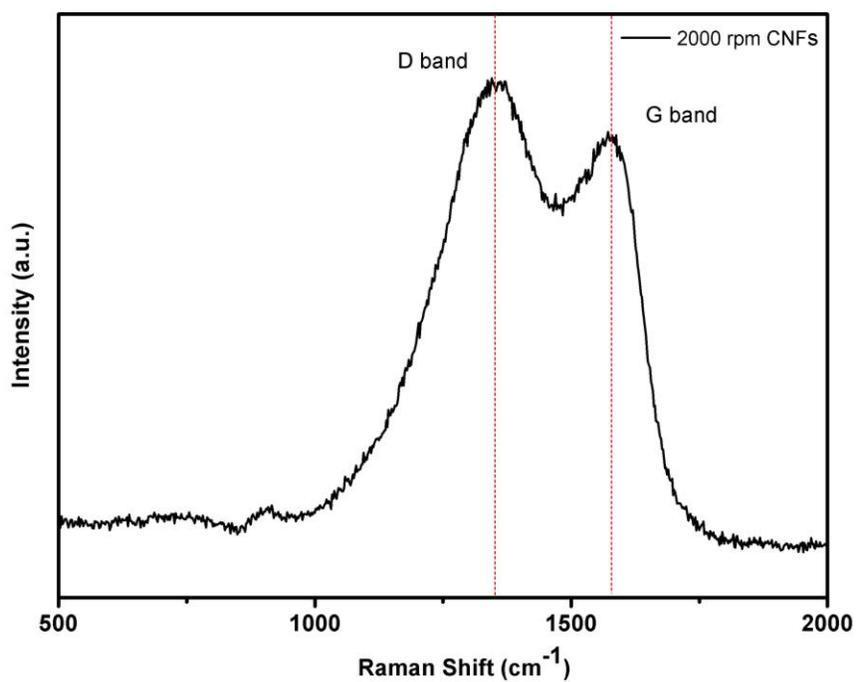


Figure S9. The Raman spectrum of before annealed CNFs prepared by electrospinning at 2000 rpm.

On the other hand, among them, the D peak represented the degree of disorder of carbon, which was the defect structure contained in the material; the G peak represented the graphite lattice vibration phenomenon of carbon atoms on the sp^2 hybrid plane. The area ratio of peak D to peak G (I_D/I_G) is usually used to describe the level of graphitization of carbon. A carbon material with a large value of I_D/I_G possesses many defect sites, which are beneficial to surface catalytic reaction. Consequently, for use as an electrochemical catalysts, 2000 rpm fabrication by electrospinning rotating collection provided more active sites for electrode reactions and accelerated electron transport.

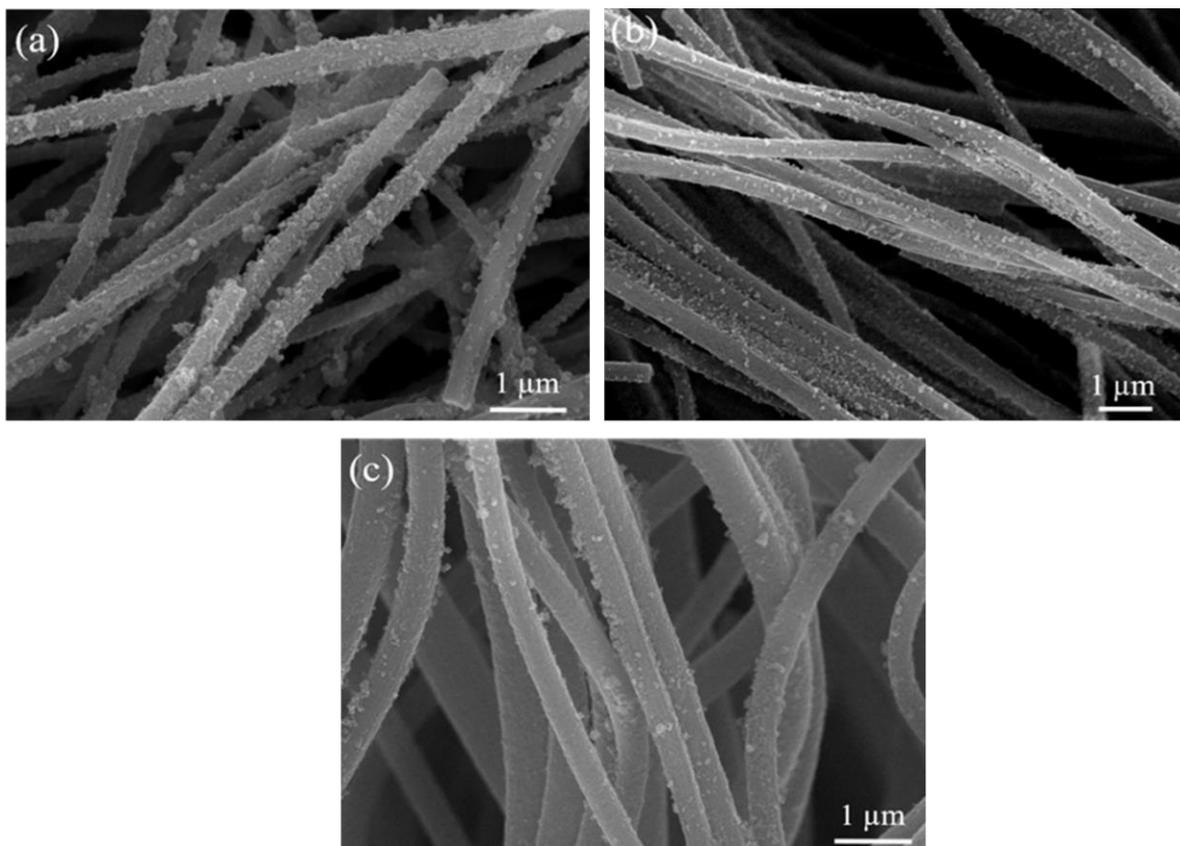


Figure S10. SEM images of (a) ZIF-8/(10mg)/CNFs composite, (b) ZIF-8/(15mg)/CNFs composite, (c) ZIF-8/(20mg)/CNFs composite prepared at normal temperature and pressure.

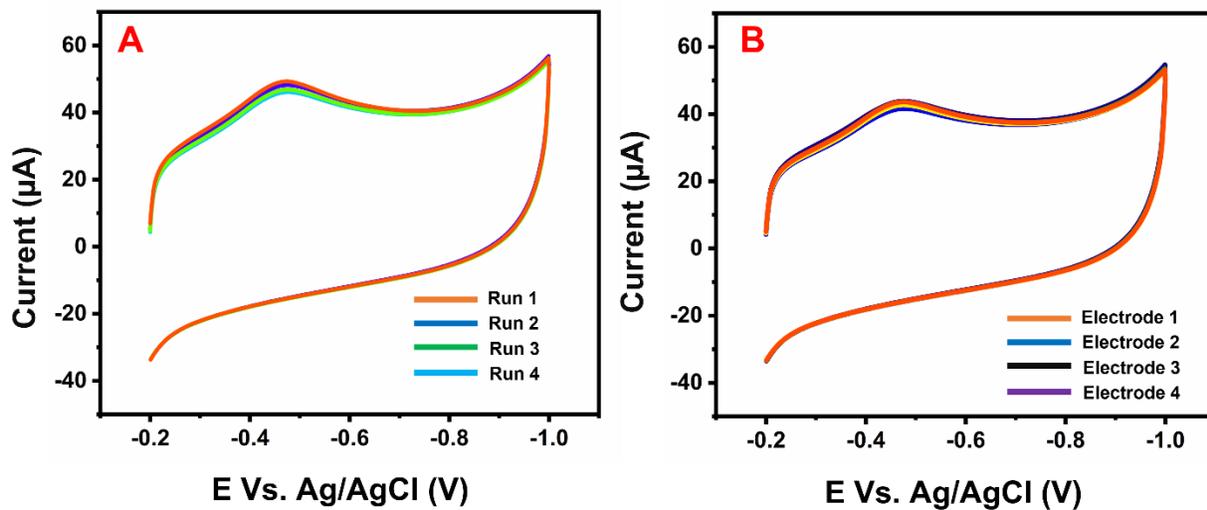


Figure. S11 (A) The CV curve of GCE/ZIF-8/CNFs electrode in the presence of the NFZ repeatability test. (B) Four different GCE/ZIF-8/CNFs electrode for reproducibility test.