

## Synergistically Enhanced Photoelectrocatalytic Degradation of Ciprofloxacin via Oxygen Vacancies and Internal Electric Field on NiSe<sub>2</sub>/WO<sub>3</sub> Photoanode.

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### **SUPPLEMENTARY INFORMATION**

#### **Materials and Method**

##### *Materials*

The chemicals employed for this study include nickel chloride hexahydrate (NiCl<sub>2</sub>·6H<sub>2</sub>O), sodium selenite (Na<sub>2</sub>SeO<sub>3</sub>), ethylene glycol (EG), sodium tungstate dihydrate (Na<sub>2</sub>WO<sub>4</sub>·2H<sub>2</sub>O), ciprofloxacin (CIP), acrylamide, Polyvinylidene fluoride (PVDF), *N*-methyl-2-pyrrolidone (NMP), sodium sulfate (Na<sub>2</sub>SO<sub>4</sub>), disodium salt of ethylenediaminetetraacetate (Na<sub>2</sub>EDTA), tert-butanol (t-BuOH), acrylamide, potassium tetraoxomanganate (VII) (KMnO<sub>4</sub>), potassium hexacyanoferrate (II) (K<sub>4</sub>Fe(CN)<sub>6</sub>) and potassium hexacyanoferrate (III) (K<sub>3</sub>Fe(CN)<sub>6</sub>). No further purification was carried out on all the chemicals obtained from Sigma-Aldrich (South Africa).

##### *Synthesis of WO<sub>3</sub> nanorods*

WO<sub>3</sub> was synthesized by dissolving Na<sub>2</sub>WO<sub>4</sub>·2H<sub>2</sub>O (2g) in 50 mL double-deionized water, followed by the addition of NaCl (0.4 g). The mixture was stirred for 30 min, and the solution was adjusted to pH 2 using 1 M HCl. The resulting white suspension was stirred for 30 min at room temperature and transferred to a Teflon-lined autoclave kept in the muffle furnace at 180 °C and held for 24 hours. The autoclave was allowed to cool naturally, and the product was collected by centrifuge and washed with water and absolute ethanol. The white solid was subsequently dried at 70 °C for 12 h.

##### *Preparation of NiSe<sub>2</sub>/WO<sub>3</sub>*

To synthesize the NiSe<sub>2</sub>/WO<sub>3</sub> heterojunction, the as-synthesized WO<sub>3</sub> (3 mmol) was dispersed in 30 mL ethylene glycol under ultrasonication until uniformly dispersed. NiCl<sub>2</sub>·2H<sub>2</sub>O (0.15 mmol) and Na<sub>2</sub>SeO<sub>3</sub> (0.3 mmol) were added to the WO<sub>3</sub> solution and sonicated for 30 min. The mixture was transferred into a Teflon-lined autoclave and maintained for 24 h at 180 °C. The product obtained at room temperature after cooling was centrifuged and rinsed with ethanol and water till a clear filtrate was obtained. The product was dried at 70 °C overnight.

### *Characterization*

A Rigaku Ultima IV X-ray diffractometer (XRD) sourced from Japan, was utilized to discern the crystalline phases within both the composite and pristine samples. The X-ray radiation source employed was Cu K $\alpha$  ( $\lambda = 1.5406 \text{ \AA}$ ), enhanced with a K- $\beta$  filter, operating at 30mA and 40 kV. To examine the shapes and constituent elements of the samples, a Field Emission Scanning Electron Microscope (FE-SEM), specifically the Zeiss Crossbeam 540 model from the United Kingdom, was employed, coupled with Energy Dispersive X-ray Spectroscopy (EDS). High-resolution images were captured using a JEM-2100 transmission electron microscope (TEM) from Japan. Electronic absorption spectra were collected using a Cary 60 UV-vis spectrometer manufactured by Agilent Technologies, located in Malaysia. Electrochemical impedance spectroscopy, Mott Schottky analysis, and photocurrent response measurements were conducted utilizing an Autolab Potentiostat workstation (PGSTAT204) from the Netherlands. The photoluminescence spectra were recorded on Shimadzu spectro fluorophotometer RF-6000

### *Fabrication of electrodes*

Fluorine-doped tin oxide (FTO) served as the substrate for electrode fabrication. The materials were deposited using the drop-casting technique. Before this, the FTO glass surface underwent cleaning via sonication in acetone for 10 minutes, followed by rinsing with water and drying at 60°C. For dispersion, 100  $\mu$ L of NMP and 5 mg of PVDF were separately mixed with 50 mg of each WO<sub>3</sub> and NiSe<sub>2</sub>/WO<sub>3</sub> sample under continuous stirring to achieve a homogeneous slurry for each dispersed sample. The conducting surface area of the FTO glass (1.7 cm x 1.7 cm) was meticulously coated with the slurry to ensure even distribution across the surface. Subsequently, the coated glass was allowed to dry in an oven at 60°C for 2 hours.

### *Photoelectrochemical study*

The PEC study utilized a conventional three-electrode cell system comprising a Pt wire (as the counter electrode), Ag/AgCl (3.0 M KCl) electrode (serving as the reference electrode), and the custom-made photoanode (acting as the working electrode). Radiation for the study was provided by a xenon solar lamp rated at 100 W. Both the incident light and the photoanode were vertically positioned, maintaining a separation distance of 10 cm. CIP degradation experiments were conducted in quartz glassware with a volume capacity of 100 mL. The electrolyte consisted of a 0.1 M Na<sub>2</sub>SO<sub>4</sub> solution containing 5 mg/L CIP. Similar experiments were repeated without light exposure to assess the electrolytic influence on degradation. The absorbance of the CIP sample was measured at intervals using a UV-vis spectrophotometer as degradation progressed.

For impedance spectroscopic analysis, the electrolyte solution was prepared by dissolving 5 mM [Fe(CN)<sub>6</sub>]<sup>3-</sup>/[Fe(CN)<sub>6</sub>]<sup>4-</sup> in a 0.1 M KCl solution. A 0.1 M Na<sub>2</sub>SO<sub>4</sub> solution was employed to determine photocurrent levels. Mott Schottky plots were generated using data obtained from experiments conducted without light exposure.

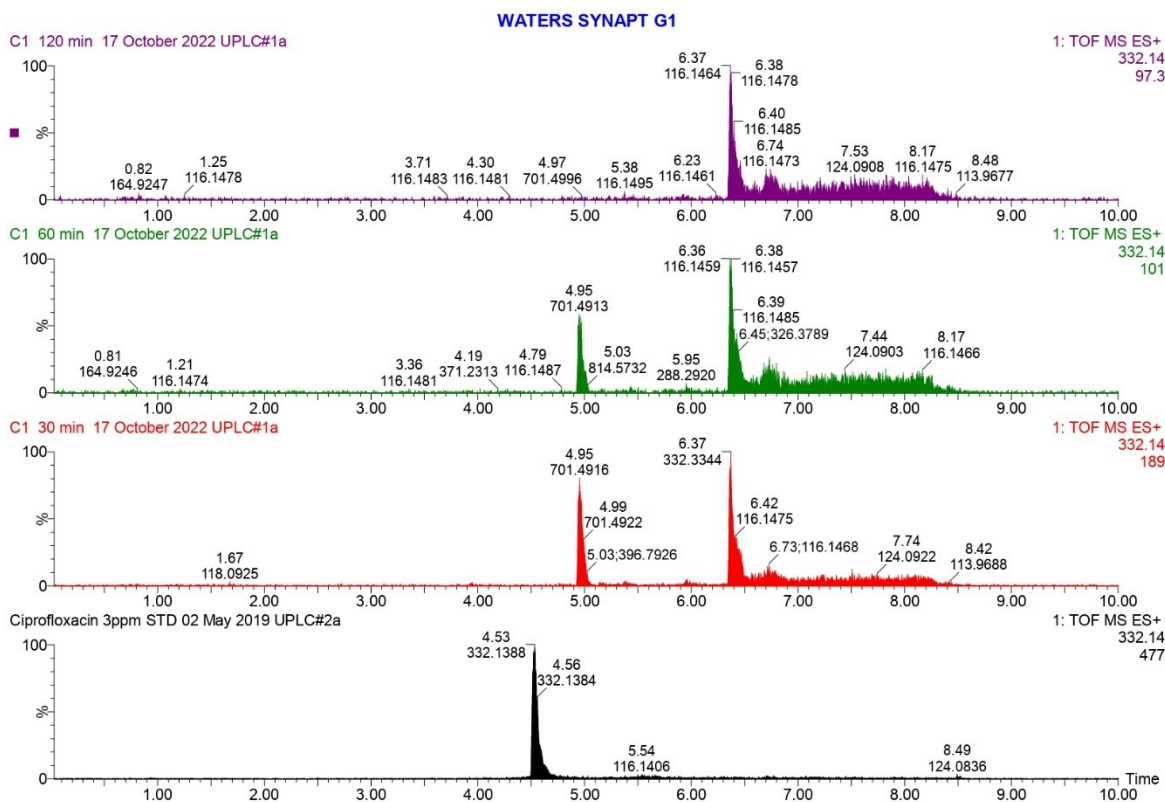


Figure 1.

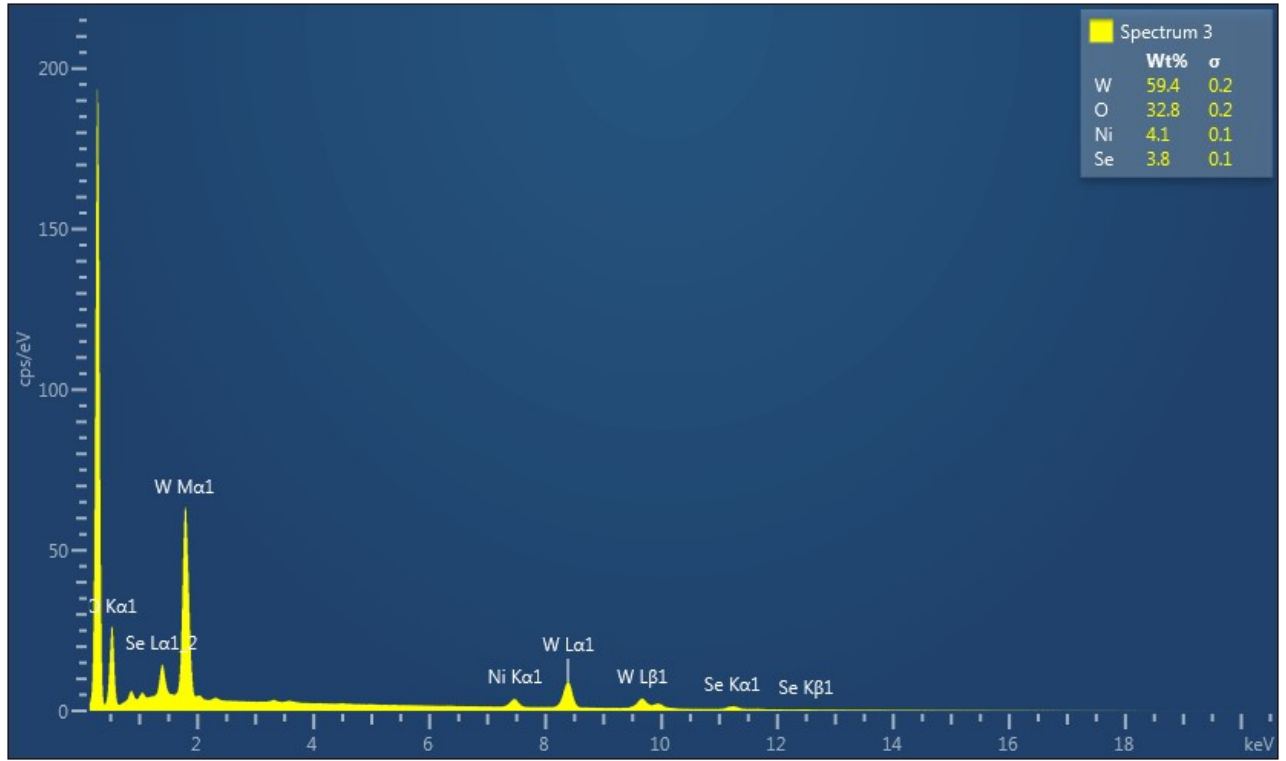


Figure 2. EDX of spectrum NiSe<sub>2</sub>/WO<sub>3</sub>