

Physicochemical Properties of Tungsten Trioxide Photoanodes Fabricated by Wet Coating of Soluble, Particulate, and Mixed Precursors

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2.4 Characterization

2.4.1 Profilometric measurements

Using a contact surface profilometer, we performed profilometric measurements to study the roughness of the coated layers. It works by making physical contact on the sample substrate using a stylus that slides across the coated surface. It can measure surface deformations and variations such as friction fluctuations and applied resistance. We started the measurement with large WO₃ particles. For samples ground for a duration of 0 to 96 hours, we set the measurement range to 64 μm, maintained a resolution of 0.666 μm for all samples, and chose the profile type as hills and the force acting on the probe at 0.5 mg. The probe had a radius of 12.5 nm. We placed the probe 0.5 mm before the beginning of the layer. In this section, we measured the so-called baseline, with which we balanced the obtained record and evaluated only the data we obtained for 1 μm of the recording path. The layer thickness was evaluated as the arithmetic mean, and its roughness as the root mean square deviation from the data was thus obtained. We repeated the measurement for the samples coated with the drop-cast method using a probe force of 0.1 mg and probe radius of 524 μm, and followed baseline correction to obtain a roughness value. As the final averaged thickness data depicted in Figures 5d, 6d, 7d were obtained from multiple measurements along a scratch running across the whole sample, their

error bars also inherently contain the information about the coatings' homogeneity.

2.4.2 Measurement of electrochemical properties

The electrochemical property can be studied by an electroanalytical method called voltammetry. This provides qualitative and quantitative information on species that involve oxidation and reduction. Voltammetry methods include cyclic voltammetry, linear sweep voltammetry, and amperometry. In voltammetry, the I v/s V plot is obtained by the supply of a time-dependent potential excitation signal to the working electrode, changing its potential relative to the fixed potential of the reference electrode. A voltogram is the resultant plot obtained from the current flow between the working electrode and the auxiliary electrode. A particular type of voltammetry is chronoamperometry. As chrono (time) and ampere (current) imply, we observe here the current dependence on time. In chronoamperometry, we choose such a voltage that the limited current passes through the system. In this measurement, the electrode's potential changes only by interactions with the analyte. We set up an electrochemical cell with a two-electrode system where the WO_3 electrode is a working electrode, and the stainless steel needle is the counter electrode. We immediately attached them to a holder made on a 3D printer, put them in a cuvette filled with electrolyte 0.1 M HClO_4 , using crocodile clips connected to the electrical circuit (FTO glass as the anode, the cathode was realized using a stainless steel needle, which also served as an air supply for electrolyte bubbling). The contribution of photocurrents was monitored by irradiating samples with a UV-A lamp from Sylvania. The voltametric curves are measured at a voltage range of -0.5 V to 2.5 V. We set a voltage of 1.5 V and a frequency of 1 Hz for the chronoamperometric measurements.

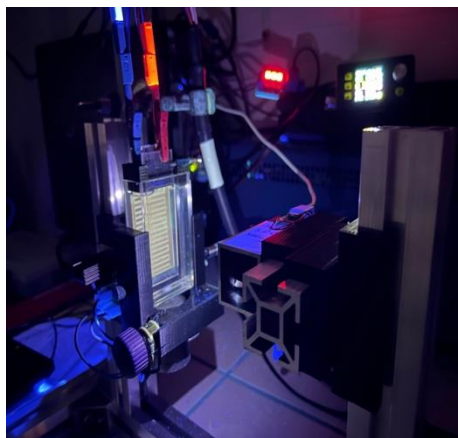


Figure S1: Pictorial representation of PEC setup.

2.4.3 X-ray diffraction (XRD)

X-ray structural analysis is a method that primarily reveals the structural and phase composition of substances. This method is non-destructive for the sample and is currently highly advanced with many data libraries. The method is suitable for applications such as qualitative and quantitative phase analysis, and determination of the structure of substances and the size of crystallites. The XRD principle is based on the impact of monochromatic X-rays. The energy of the incident radiation is the same as the energy of the reflected radiation. For the interference to occur, the Bragg condition should be met as follows:

$$n \cdot \lambda = 2 \cdot d \cdot \sin \theta \quad [\text{Bragg equation}] [62].$$

where n is an integer and corresponds to the order of diffraction, λ is the X-ray wavelength, d is the interplanar distance, and θ is the angle of radiation incident on the structural plane. Suppose the Bragg condition is met, and the reflected rays are parallel: in this case, interference will occur. The so-called diffraction maxima will occur, which are position, shape, and intensity, depending on the type and arrangement of the atoms in space, and are specific to each substance. XRD instrumentation consists of a radiation source, a monochromator, a goniometer, and a detector. The source is usually realized using a vacuum tube, in which two electrodes are placed, to which a voltage (20–60 kV) is applied. The cathode emits electrons that are accelerated by a high voltage and impinge on the anode. Most of the kinetic energy of these electrons converts to thermal energy (98–99%), and the rest is emitted as X-rays. The monochromatic radiation then impinges on a sample

placed in the goniometer, rotating at a constant speed. Thus, there is a smooth change in the size of the angle of the incident radiation. The radiation reflecting from the sample falls on the detector, which records its intensity depending on the angle of incident radiation on the sample. For a specific substance, the so-called constructive interference occurs at a certain angle, which manifests itself as a peak in the resulting diffractogram [63–65]. The XRD analyses were carried out with an Empyrean diffractometer from the Malvern-PANalytical Corporation. The measurement parameters were as follows: tube current 30 mA and voltage 40 kV; anode material Cu ($K\alpha_1 = 1.540598 \text{ \AA}$); step size 0.01313 \AA ; time per step 33 s. The results were evaluated using the software HighScore plus.

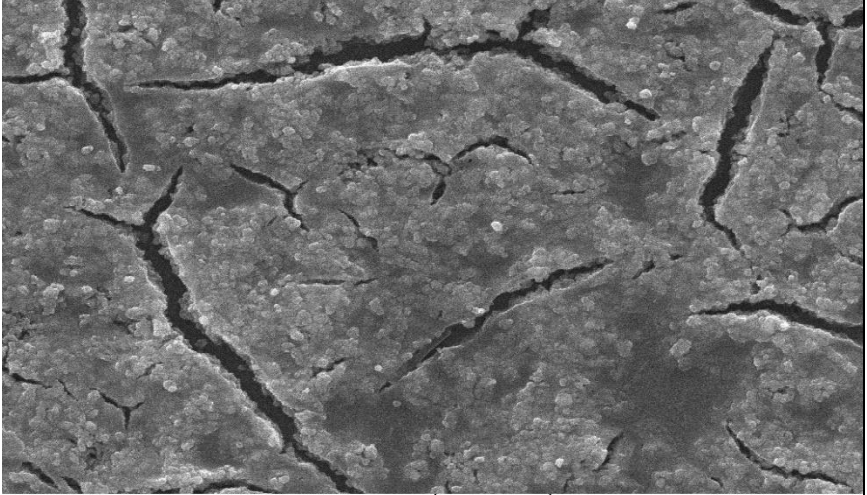
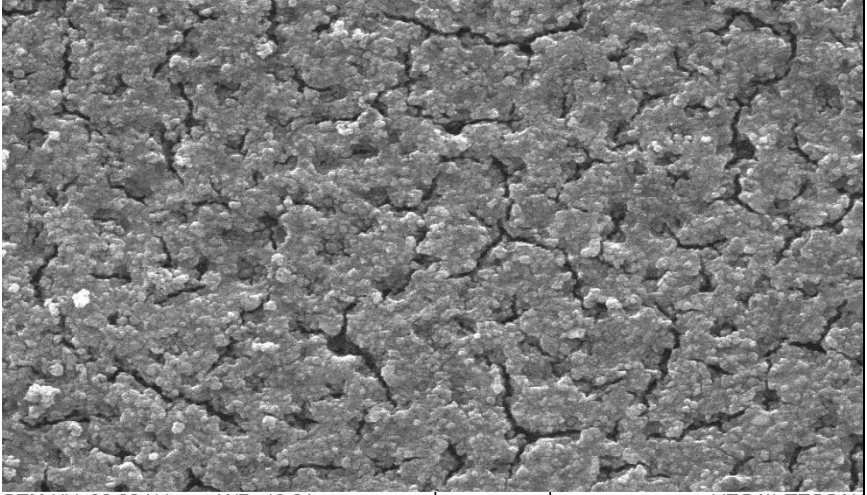
2.4.4 Scanning Electron Microscope

A scanning electron microscope (SEM) uses a beam of high-energy electrons to generate various signals at the surface of materials. The signals that are derived from the interaction of the samples and electrons provide information on the sample morphology, composition of the material, crystalline structure, and material orientation. In most applications, data are collected over a selected area of the sample's surface, and the generated 2D image displays spatial variations [66]. The samples are mounted on the SEM stage, and they are masked with copper foil, to reduce the charging. The morphology of all the prepared inks is measured using scanning electron microscopy (refer to Table S1 and Table S2 for the operating voltages used for the measurements).

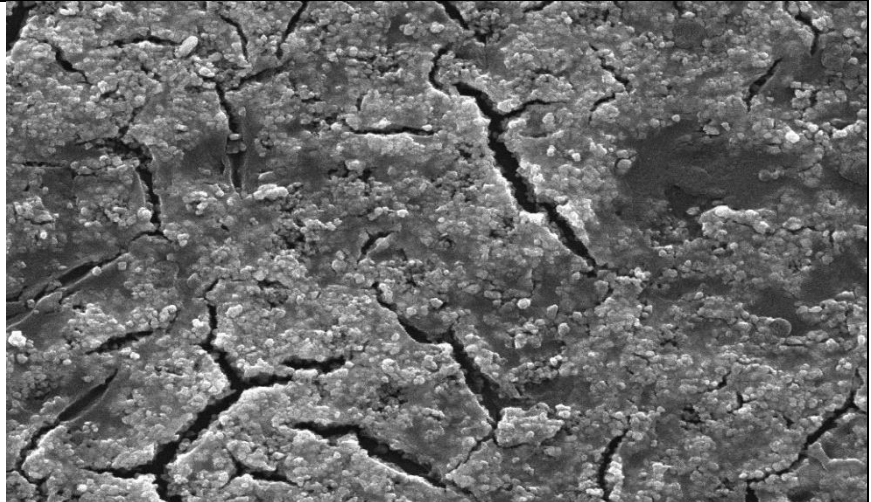
Table S1: The operating voltages used to measure the morphology of WO_3 particles, APTA, and brick-and-mortar ink.

Inks	Operating voltage
WO_3 particles	30.0 kV
APTA	30.0 kV
Brick-and-mortar	30.0 kV

Table S2. Microscopic images of prepared WO₃ particles, APTA and brick-and-mortar inks.

Inks	Scale in the range of 2-5µm
WO ₃ particles	 <p>SEM HV: 30.00 kV WVD: 13.08 mm View field: 15.08 µm Det: SE Detector SEM MAG: 20.00 kx Date(m/d/y): 01/03/24</p> <p>2 µm</p> <p>VEGA\\ TESCAN FCH</p>
Acetylated peroxotungstic acid (APTA)	 <p>SEM HV: 30.00 kV WVD: 13.01 mm View field: 15.08 µm Det: SE Detector SEM MAG: 20.00 kx Date(m/d/y): 01/03/24</p> <p>2 µm</p> <p>VEGA\\ TESCAN FCH</p>

**Brick-and-
mortar**



SEM HV: 30.00 kV WD: 13.12 mm
View field: 17.40 μ m Det: SE Detector
SEM MAG: 17.33 kx Date(m/d/y): 01/03/24

5 μ m VEGA\\ TESCAN
FCH

2.4.5 Thermogravimetric Analysis

Thermogravimetric analysis is one of the simplest and most basic methods of thermal analysis. It studies system changes, such as weight, volume, conductivity, and energy increase or decrease. These properties are studied as a function of temperature. The result of such measurements are thermogravimetric curves, which show the dependence of weight loss on time or temperature. They provide information not only about the course of thermal decomposition and the stability of the sample, but also about the decomposition of products.