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**O1 & O2A; Laboratory reports on synthesis, preparation, immobilization
and characterization of photocatalytic materials (D1.1, D1.2, D1.3, D1.4 and
D2.1)**

Project: Solar-assisted photocatalytic degradation of perfluorinated compounds in water
(*SoAPperF*), IPS-2002-02-4780.

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1. Experimental procedure for obtaining photocatalysts and co-catalyst materials

Indium oxide (In_2O_3)

Pure In_2O_3 was synthesized by dissolving 1.59 g of $\text{In}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$ into a 100 mL mixed solution of water and ethanol (70:30 v/v) followed by the addition of 1.80 g of urea and 0.36 g of CTAB, respectively. The resulting sample solution was stirred on a magnetic stirrer with a stirring speed of 600 rpm for 50 min. Thereafter, the obtained clear solution was transferred in a Teflon vessel, sealed tightly and kept at 170 °C for 12 hours. Afterward, the sample was cooled to room temperature and centrifuged at 4000 rpm. The solid product was washed thoroughly with water followed by ethanol, and then dried at 65 °C. The dried white powder was further calcined in a muffle furnace for 2 hours at 500 °C resulting to which a yellowish (pale yellow) colored In_2O_3 was obtained.

Strontium titanate and iron-doped strontium titanate (SrTiO_3 , Fe- SrTiO_3)

To prepare SrTiO_3 , 2.116 g of $\text{Sr}(\text{NO}_3)_2$ and 3.4 g of $\text{Ti}(\text{OBu})_4$ were dissolved in 50 mL of water (Solution A) and ethanol (Solution B), respectively, in a 1:1 molar ratio. Solution A was then added to Solution B while stirring continuously at 700 rpm. After mixing, 20 mL aqueous solution of 5 M NaOH was added to the resulting solution and stirred for 20 minutes. The mixture was transferred to a hydrothermal reactor and placed in a hot air oven at 200 °C for 16 hours. Afterward, the sample was cooled to room temperature and centrifuged at 4000 rpm. The solid product was washed thoroughly with water followed by ethanol, and then dried at 65 °C. Fe-doped SrTiO_3 was synthesized following the SrTiO_3 hydrothermal procedure, with $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ used as the iron source. $\text{Sr}(\text{NO}_3)_2$ was dissolved in water (Solution A) to prepare a 0.2 M strontium precursor, while $\text{Ti}(\text{OBu})_4$ was dissolved in ethanol (Solution B) at a concentration adjusted to achieve the desired Fe/Ti molar ratio. The required amount of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ was calculated based on the targeted composition and added to Solution A. Under continuous stirring at 700 rpm, Solution A containing Sr and Fe precursors was added to Solution B. After homogenization, 20 mL of 5 M NaOH was introduced, and the mixture was stirred for an additional 20 min. The suspension was then transferred to a Teflon-lined hydrothermal reactor and heated at 200 °C for 16 h. After cooling to room temperature, the product was collected by centrifugation at 4000 rpm, washed repeatedly with water and ethanol, and dried at 65 °C.

Graphene oxide (GO)

A modified Hummers method was used in which graphite (3 g, mesh <100) was mixed with 69 mL of cooled 97% H₂SO₄ and 1.5 g of dry NaNO₃ in an ice bath while maintaining the temperature at 0 °C under constant stirring in a round-bottom flask. KMnO₄ (9 g) was then added slowly, ensuring the temperature remained below 20 °C, and the mixture was stirred while keeping the temperature at or below 35 °C for 30 min. After 1 h of total stirring, 138 mL of DI water was added slowly, ensuring the temperature did not exceed 98 °C. The mixture was cooled to room temperature and diluted with 1 L of DI water without stirring. Subsequently, 30% H₂O₂ was added gradually until effervescence ceased. The obtained dispersion was washed with 5% HCl to remove MnO₂, followed by repeated water washing in a centrifuge until the supernatant reached near-neutral pH. The product was then sonicated for 1 h in an ultrasonic cleaner to exfoliate the material, dialyzed for 3 weeks using a Spectrum-Pore membrane to remove remaining impurities, and finally vacuum-dried at 35 °C for 4 weeks.

Carbon quantum dots from lignin (CQD)

Lignin (0.300 ± 0.005 g) was dispersed in 30 mL of Milli-Q water in a round-bottom flask and sonicated for 20 min, ensuring that the ultrasonic bath did not overheat; the bath water was replaced if necessary to maintain a stable temperature. Hydrochloric acid was then added (either 20 μ L or 1 mL, depending on the experimental condition), and the suspension was stirred for 30 min once the temperature reached 60 °C, with the flask connected to a condenser. After this period, the condenser was removed and 0.3 g of 3-aminoboronic acid was added as the dopant. The mixture was stirred continuously and heated to 90 °C; after reaching this temperature, stirring was maintained for 1 h. The reaction mixture was subsequently allowed to cool to room temperature while stirring for approximately 15 min. The suspension was then filtered through a 0.45 μ m nylon membrane and transferred into a Teflon-lined hydrothermal reactor, where it was heated at 200 °C for 10 h. The following day, the product was filtered twice through a 0.22 μ m nylon membrane. Dialysis tubing was rinsed with distilled water and filled with the filtered sample, followed by dialysis for a minimum of 48 h with periodic replacement of the external water. The final concentration of the obtained solution was determined gravimetrically. At the end of the procedure, the CQDs were lyophilized.

Graphitic carbon nitride (g-C₃N₄)

Melamine (13 g) was placed in an alumina crucible and calcined in a muffle furnace at 550 °C for 4 h to obtain bulk g-C₃N₄, which was then ground thoroughly in a mortar. To prepare exfoliated g-C₃N₄ nanosheets, 5 g of the bulk material was dispersed in 30% H₂SO₄ and stirred for 22 h. The resulting suspension was sonicated for 1 h, followed by centrifugation and thorough washing with water and ethanol. The washed product was dried at 65 °C under vacuum for 24 h to obtain g-C₃N₄ nanosheets.

Copper (I) oxide (Cu₂O)

To prepare Cu₂O, Copper acetate monohydrate (Cu(CH₃COO)₂×H₂O) and D-glucose was mixed in 120 mL of water in 1:1 molar ratio. After that 1.093 g of CTAB was added in the mixed solution as a stabilizer. The resulting solution was taken in a Teflon lined stainless steel vessel, sealed tightly and was kept inside an oven for 12 h at 100 °C. The sample was cooled at room temperature and centrifuged at 4000 rpm, the collected solid sample was washed with water and ethanol to remove any unwanted impurities. Then it was dried under the vacuum at 60 °C for 24 h.

Silver phosphate (Ag₃PO₄)

Synthesis 2: 2.718 g of anhydrous AgNO₃ was dissolved in 80 mL of water to prepare solution A. Solution B was prepared by dissolving 1.136 g of Na₂HPO₄ in 40 mL of water. Hereafter, solution B was added drop wise into solution A with stirring, yellow colour precipitate was obtained. The stirring was continued for 10 minutes. The pH of precipitated solution was adjusted at 6 by adding HCl or NaOH. After that, the sample was filled in an autoclave and placed in an oven at 120 °C for 6 h. The resulting sample was allowed to cool, centrifuged, washed well with water. The solid yellow slurry was dried at 70°C in an oven.

Composite Cu₂O/Ag₃PO₄

119.8 mg of as prepared Ag₃PO₄ was dispersed ultrasonically in 120 mL of water for 25 minutes. In the dispersed solution, Cu(CH₃COO)₂×H₂O and D-glucose were added in equimolar ratio (1:1) followed by the addition of CTAB (0.025 M). The sample was continuously stirred for 20 minutes then transferred into a teflon lined autoclave. The tightly sealed autoclave was kept in oven at 100 °C for 12 h. The resulting sample solution was

centrifuged and washed with water and ethanol to remove any kind of impurity if present. The collected solid sample was dried in a vacuum oven at 60 °C for 24 h.

Composite C₃N₄/Fe-SrTiO₃

200 mg of g-C₃N₄ (exf.) was dispersed in 50 mL of water and sonicated for 30 minutes in an ultrasonic cleaner, in the resulting colloidal solution 2.116 g of Sr(NO₃)₂ was dissolved (solution A). Another solution was prepared by the subsequent addition of 3.30 g and 0.122 g of Ti(OBu)₄ and FeN₃O₉×9H₂O in 50 mL of ethanol (solution B). Thereafter, solution A was added to solution B followed by the addition of 5 M of 20 mL NaOH with continuous stirring. After 20 minutes of stirring, the mixed sample was poured into a Teflon lined autoclave and heated at 200 °C for 16 hours. The autoclave was cooled down and the obtained sample was centrifuged and washed four times with water and two times ethanol. The resulting slurry was dried under the vacuum at 65 °C.

Composite CQD-In₂O₃

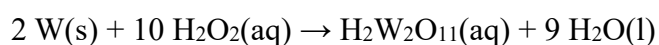
For the preparation of the composites, In₂O₃ was used along with CQDs employed in their liquid form. The concentration of the CQD dispersions had been previously determined gravimetrically (Type 1: 20 µL HCl CQD: 0.175 mg/mL, total volume 16 mL; Type 2: 1000 µL HCl CQD: 0.125 mg/mL, total volume 20 mL). For the preparation of the 0.03 CQD–In₂O₃ composite, In₂O₃ and CQD dispersions were used as follows: (i) 16 mL CQDs (20 µL HCl route) were combined with 90.53 mg In₂O₃; or (ii) 20 mL CQDs (1000 µL HCl route) were combined with 80.83 mg In₂O₃. In₂O₃ powder was dispersed in a glass flask in 20 mL of ethanol. The suspension was sonicated for 15 min, while CQDs were separately sonicated for 15 min in glass vials. Subsequently, the In₂O₃ suspension was heated to 40 °C and stirred at 200 rpm (avoiding vortex formation), with the flask wrapped in aluminum foil. CQDs were added dropwise over 30 min (one drop every ~4 s). After the complete addition of CQDs, the temperature was increased to 90 °C and the mixture was stirred at 200 rpm until nearly all solvent had evaporated. The resulting material was then calcined at 300 °C for 3 h. In the end, the composites were washed twice with water, twice with ethanol, and dried 65 °C for 3 h.

Composite rGO-In₂O₃

The rGO-In₂O₃ composites were synthesized as follows. In₂O₃ nanoparticles (200 mg) were dispersed in 10 mL of water and sonicated for 10 min to obtain a uniform suspension. Separately, 1 mg (for 0.5% rGO-In₂O₃) or 3 mg (for 1.5% rGO-In₂O₃) of graphene oxide (GO) was dispersed in 10 mL of water by sonication for 10 min to form a homogeneous GO dispersion. The In₂O₃ suspension was then combined with the GO dispersion, stirred for 5 min, and subsequently sonicated for 4 h. The resulting mixture was heated to 95 °C under vigorous stirring. Hydrazine solution (40%, 9 µL) and ammonia solution (25%, 70 µL) were then added to the mixture. After 1 h of stirring, the suspension was filtered, washed with water and ethanol, and dried at 100 °C for 12 h.

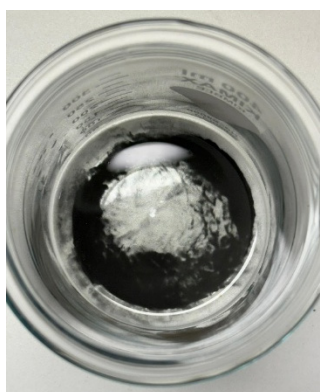
WO₃ and WO₃ modified by Zn and Ga

Electrochemical synthesis of WO₃ photocatalysts, peroxotungstic acid (H₂W₂O₁₁) was carried out by dissolving tungsten powder (0.95 g) in 10 mL of 30% hydrogen peroxide, H₂O₂, according to the reaction:



The dissolution of tungsten powder lasted about 60 min. After complete dissolution, the excess peroxide was decomposed using a platinum mesh catalyst, which was left overnight (Figure 1). The solution was quantitatively transferred and diluted to 25 mM in a mixture of water and 2-propanol in a ratio of 70:30. The pH of the initial mixture was approximately 1.9, and the acidity of the final precipitation solution was adjusted to pH 1.1 by adding 2 – 3 mL of 5% nitric acid.

(a)



(b)



Figure 1. a) dissolving tungsten powder in hydrogen peroxide and b) the reaction of the remaining hydrogen peroxide at Pt mesh

A three-electrode system (working electrode-FTO glass, Pt counter electrode and reference electrode-SCE) was used for the electrodeposition of WO_3 on FTO slides. WO_3 films were electrochemically deposited on FTO slides, which were previously cleaned with ethanol, acetone and redistilled water in an ultrasonic bath for 10 minutes. The area 2 cm^2 was immersed in a peroxotungstic acid solution, and the electrodeposition process was carried out at $E = -0.645 \text{ V}$ without stirring for 10 and 20 min (Figure 2).



Figure 2. Three-electrode system for electrodeposition of WO_3 and modified WO_3

After film deposition, the WO_3 electrode was annealed at $500 \text{ }^\circ\text{C}$ for 2 hours in an oven and left to cool overnight. The electrodes of modified WO_3 were prepared in the same way, with the addition of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ of different masses, which are $m_1 = 0.0925$ (sample 3) g and $m_2 = 0.2770$ g (sample 4). Sample 5 was prepared from the solution in which the electrochemical synthesis of modified WO_3 was carried out, the oxide was precipitated by the sol-gel process. Sample 6 was synthesized electrochemically, similar as sample 2 and in addition $100 \text{ }\mu\text{L}$ of the synthesis solution containing W- and Zn- salts was drop casted over sample 2.

Table 1. Name of samples

Electrode	Composition
Sample 1	WO_3 – synthesis 10 min
Sample 2	WO_3 – synthesis 20 min
Sample k 3	modified WO_3 ($0.0925 \text{ g Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$)
Sample 4	modified WO_3

	(0.277 g $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$)
Sample 5	modified WO_3 sol-gel
Sample 6	modified WO_3 + drop casting

WO_3 electrodes modified with gallium were prepared by adding a certain mass of GaCl_3 to the solution before electrodeposition onto FTO slides, after which the solutions were left on a stirrer for 30 minutes. The mass of GaCl_3 was 0.220 g. The electrodeposition of these electrodes was carried out in the same way as the electrode of pure WO_3 . The obtained electrodes are shown in Figure 3.

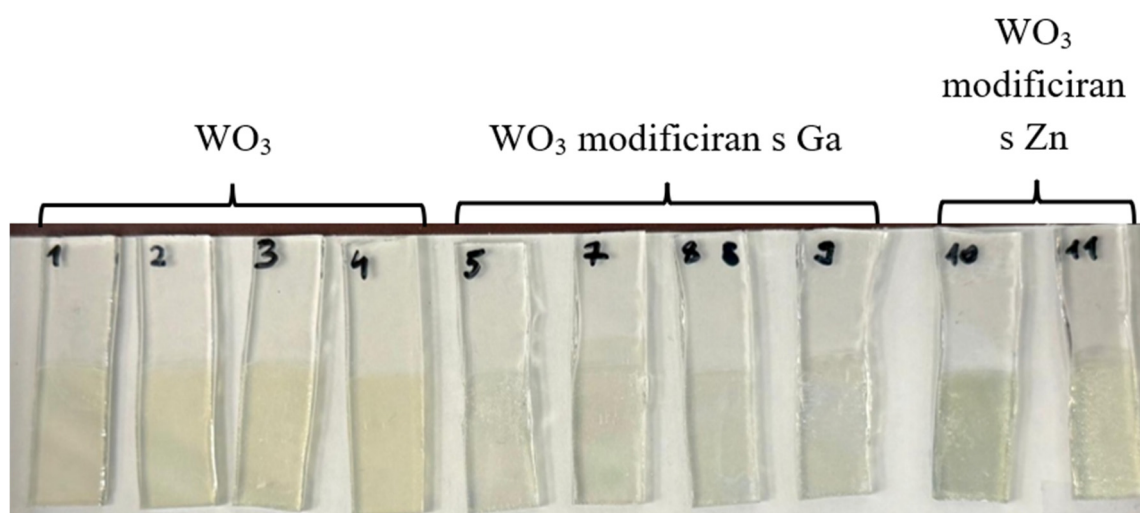


Figure 3. Electrodes obtained by the chronoamperometry method

The second set of electrodes was prepared by electrodeposition using the chronocoulometry (CC) method at a potential of $E = -0.645$ V and a charge of $Q = 7020$ mC, in order to deposit films of equal thickness depending on the charge. Two masses of GaCl_3 were added, i.e. for 10% GaCl_3 the mass was 0.073 g, and for 5% GaCl_3 the mass was 0.037 g. The resulting electrodes are shown in Figure 4.

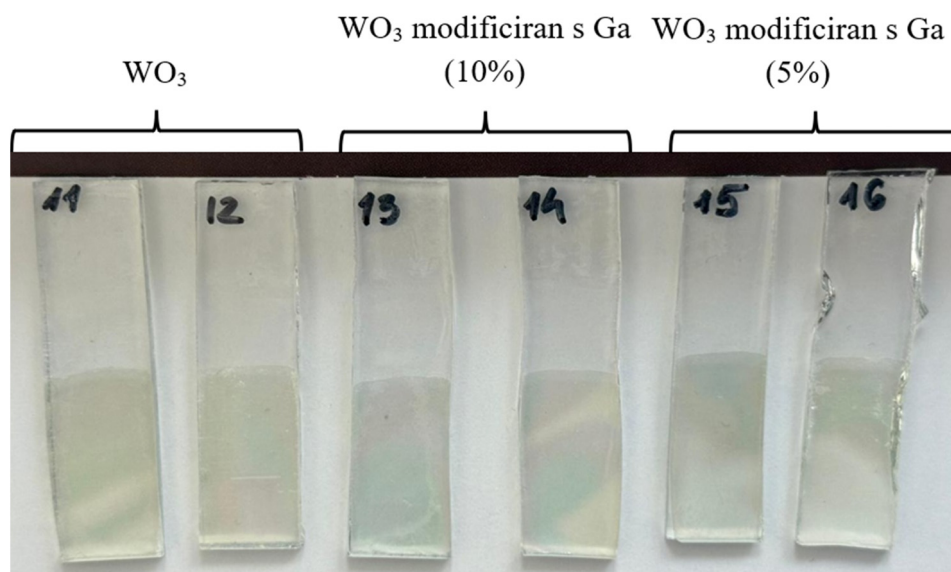


Figure 4. Electrodes obtained by chronocoulometry method

Table 1. List of samples

Electrode	composition
Sample 1	WO ₃ (CA)
Sample 2	modified WO ₃ – 32% (0.220 g GaCl ₃)
Sample 3	modified WO ₃ – 40% (0.277 g Zn(NO ₃) ₂ ·6H ₂ O)
Sample 4	WO ₃ (CC)
Sample 5	modified WO ₃ – 10% (0.073 g GaCl ₃)
Sample 6	modified WO ₃ – 5% (0.037 g GaCl ₃)

TiO₂ modified by Pt

We prepared platinum-modified titanium dioxide (TiO₂) as a photocatalyst for the degradation of PFOA. Titanium dioxide without platinum modification was prepared by a particulate sol-gel synthesis from titanium tetrachloride (TiCl₄) precursor. 3.68 mL of TiCl₄ were dissolved in a solution, containing 60 mL of distilled water and 4.95 mL of 12 M H₂SO₄. After one day

of stirring, 0.3 mass % of hydroxypropyl cellulose (HPC, relative to the total mass of the solution) was added. The sample was then doped with 2.0 mol % of NH_4NO_3 (relative to TiO_2), obtaining the unmodified TiO_2 sample (sample name TiO_2). Finally, 1.0 mol % of H_2PtCl_6 (relative to TiO_2) was introduced to obtain the Pt-modified TiO_2 sample (sample name Pt- TiO_2). The prepared sols were then dried in an oven at 100 °C for 12 h to produce xerogels, which were then calcinated in a muffle furnace at 600 °C for 1 hour to obtain crystalline, photocatalytically active TiO_2 . To prepare Pt-modified commercial TiO_2 (P25), 200 mg of P25 was dispersed in 20 mL of ethanol and stirred for 10 minutes. Then, 1 mL of an H_2PtCl_6 precursor solution was added, and the mixture was stirred for an additional 30 minutes to achieve homogeneous impregnation. The resulting suspension was dried at 90 °C and subsequently calcined at 450 °C for 30 minutes.

Immobilized S3N2

1.2 Synthesis of materials

The catalyst S3N2 was synthesised by dissolving 3.68 mL of TiCl_4 in a solution of 60 mL of distilled water and 3.3 mL of 18 M H_2SO_4 . A magnet was added to the beaker and let it stir on the magnetic stirrer for at least 12 hours. After a day, we added 0.3% (v/v) hydroxypropyl cellulose to the solution, which amounted to 217 mg. When it dissolved, we added another 2 mol.% of NH_4NO_3 (relative to the amount of TiO_2), which amounted to 53.7 mg. We then air-dried this solution until it completely evaporated and became a gel, then put it in the oven at 90 °C for 1 hour, turning the gel black. We scratched the gel out of a petri dish and transferred it to a ceramic dish. The gel was then thermally treated in an oven at 600 °C for one hour. After an hour, I took it out of the stove, let it cool and moved it to a plastic container for storage.

1.3 Synthesis of binder (Binder 2)

3.33 mL of TEOS (Tetraethyl orthosilicate) was mixed with 5.1 mL of colloidal SiO_2 (Levasil 200/30), 97 μL HCl (30%) and 15 mL isopropanol. The beaker was placed on a magnetic stirrer with a magnet in the beaker, covered with parafilm and let stirring for 24 hours.

1.4 Synthesis of binder (Binder 3)

We mixed 3.33 mL of TEOS (Tetraethyl orthosilicate), Na_2SiO_3 (water glass), 96.8 μL of 30% HCl and 15 mL of isopropanol into a beaker. The beaker was placed on a magnetic stirrer and left stirring covered with parafilm for 24 hours.

1.5 Synthesis of PR0, PR1, PR2 and PR3

To prepare the composites, we used the same process for all four, with only the amounts of chemicals listed in Table 2 differing. We added Binder 2, S3N2, 1-propanol, and then ethylene glycol to the beaker in order, except for PR0. We stirred this solution for a few minutes to 30 min and placed it in an ultrasonic bath to ensure it was homogeneous.

Table 1: Composition of composite catalysts

	PR0	PR1	PR2	PR3
<i>Binder 2 (120 g/L, mL)</i>	5	5	8.335	5
<i>S3N2 (237 g/L, mL)</i>	5	5	8.335	5
<i>1-propanol (mL)</i>	10	10	4.168	4
<i>Ethylene glycol (mL)</i>	0	10	4.168	6
<i>Surface density 4 layers on glass (mg/cm^2) *</i>	-			0.267
<i>Surface density 4 layers on SS (mg/cm^2) *</i>	-			0.254
<i>Success</i>	✗	✓	✓	✓

* The layers on glass and stainless steel (SS) were prepared by dip-coating.

1.6 Immobilization

The first immobilization technique used was dip-coating which was applied to substrates made of glass and stainless steel (SS, Fig. 1). The substrates were cut to dimensions of $12 \times 75 \text{ mm}^2$. We poured the composite catalyst from a beaker into a tube wide and deep enough to fully submerge the substrate. We inserted a substrate into the slider and aligned it with a test tube attached for stability. At a speed of 10 cm/min, the individual stainless steel and glass substrates were moved into the composite catalyst suspension. Once the substrate was removed from the suspension, we carefully grasped it from the side, avoiding disturbance of the applied

layer, and placed it on a metal stand to air dry. We then placed this rack in the oven at 150 °C and allowed each layer to dry for 30 minutes. After the time had elapsed, we removed the rack with the coated substrates, waited for it to cool, and repeated the dip-coating process as many times as necessary. The best results were obtained with 4 coatings, after that the films were mechanically unstable. The final coated surface area was $12 \times 70 \text{ mm}^2$ per side, thus effectively $24 \times 70 \text{ mm}^2$.

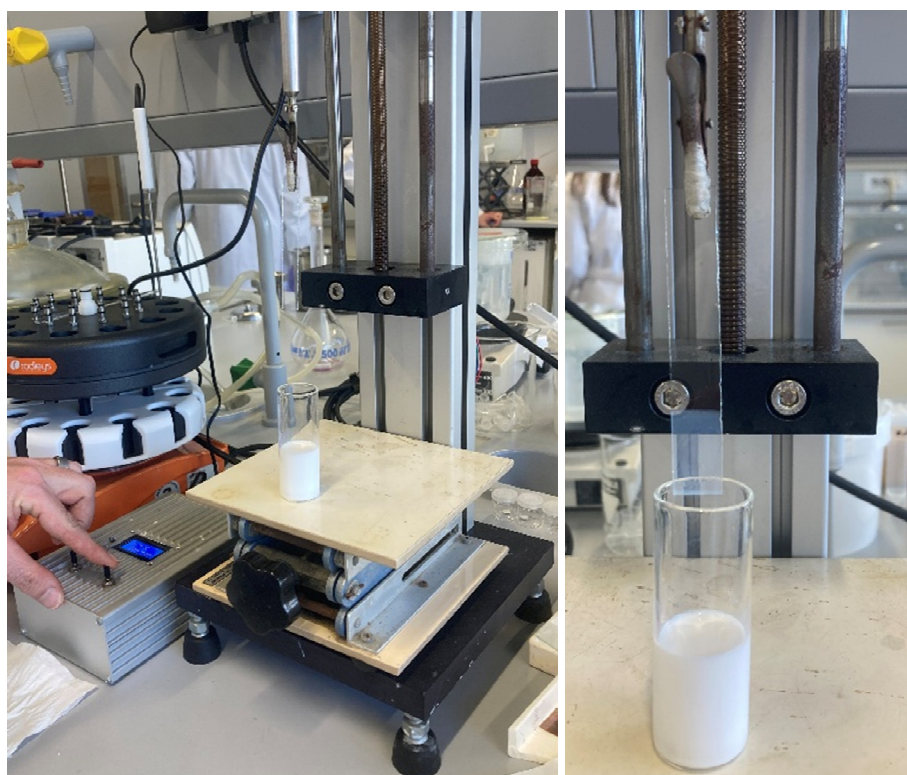


Figure 1: Dip-coating apparatus

The second immobilization technique was doctor-blade coating (Fig. 2), which was used only on polymer substrates (PET foil). On the apparatus (Neurtek. Spain), we attached a piece of polymer in an approximate size of $60 \times 120 \text{ cm}^2$ with the spring attached. We installed a threaded Meyer rod with a $25 \mu\text{m}$ groove on top of the clamped polymer and applied $200 \mu\text{L}$ of composite catalyst suspension evenly to the rod with a pipette. Immediately after that, at a speed of 50 mm/s , we coated the plastic to create a wet layer. We then dried the coated polymer in the oven at $90 \text{ }^\circ\text{C}$ for 30 minutes. Then we took it out, waited for it to cool down and made another layer on the other side and dried it again in the dryer. We repeated this as many times as necessary. Finally, we then heated the plastic to $130 \text{ }^\circ\text{C}$ for 2 hours so that the ethylene glycol

completely evaporated from the layer. For the application we coated 3 cycles which resulted in the surface density of around 0.4 mg/cm^2 . Such films were then cut into strips ($12 \times 75 \text{ mm}^2$) in order to be placed into the photocatalytic reactor cell (see below).

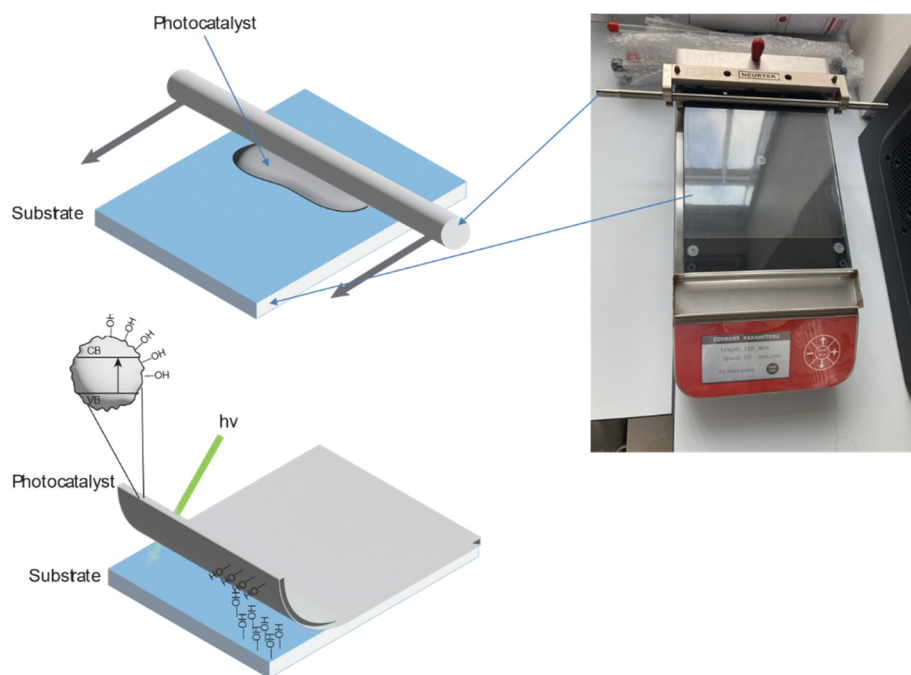


Figure 2: Doctor-Blade coating apparatus (right) and schematic representation of formation of coatings (left)

2. Characterization and evaluation of synthesized photocatalyst properties

METHODS

Optoelectronic properties determination

Photoelectrochemical measurements (PEC)

OCP measurements were carried out to assess the light response of the photocatalyst and to quantify the photopotential which reflects the charge accumulation and relaxation dynamics of a photoelectrode coated with photocatalytic material. Several different photoelectrochemical measurements (PEC) were conducted; Open Circuit Potential (OCP), Impedance Spectroscopy (EIS) in fixed mode (Mott-Schottky analysis) and scan mode (Nyquist analysis) frequency, as well as Chromoaperometry (CA) and Linear Sweep Voltametry (LSV). All PEC measurements were done using a potentiostat/galvanostat (SP-150, Biologic, France) and a LED light source, corresponding absorption spectra can be find in our previous study. All PEC measurements were performed in 0.5 M solution of sodium sulphate in a three-electrode system, consisting of a platinum counter electrode, calomel reference electrode and working electrode in the form of a fluorine-doped tin oxide (FTO) glass (1 cm²) coated with the photocatalytic material. The immobilization of the photocatalytic materials on FTO glass in the form of three thin layers was done using spin coating method (KW-4 A spin coater, Chemat Technology, USA) and titania/silica binder which procedure was published in previous paper. LSV measurements were carried out with a scan rate of 20 mV/s under the light illumination and in the dark coonditions. EIS measurements were carried out in the dark conditions (Mott Schottky) where frequency was fixed at 3000 Hz and under the illumination (Nyquist) where the frequency range was scanned from 100 kHz to 100 mHz at OCP and dc potential of 0 V with amplitude of ± 5 mV. CA measurement was done for 300 seconds under continuous UV illumination and constant potential of 0.5 V to evaluate the photocatalytic current response over time.

UV-Visible Diffuse Reflectance Spectroscopy (UV-VIS DRS)

The diffuse reflectance measurements were taken on powdered samples using a UV-Vis spectrometer 2600i (Shimadzu, Japan), equipped with an ISR-2600Plus integrating sphere.

Photoluminescence (PL) spectra

PL analysis was conducted at room temperature using Varian Cary Eclipse fluorescence spectrophotometer (Agilent, USA) with excitation wavelengths between 395 and 430 nm.

Surface, structural and morphology properties determination

The crystal structures of the samples were analyzed by X-ray diffractograms (XRD) acquired by using a RigakuMiniflex 600 (Tokyo, Japan) instrument with a Cu K α target at 40 kV and 10 mA. Scanning electron microscope (SEM) equipped with energy dispersive X-ray spectroscopy (EDS) was used to determine the morphology, and elemental composition of the material. Transmission electron microscopy (TEM) using Cs probe corrected STEM JEOL ARM 200 CF (Japan) with the cold-FEG cathode was also used to elucidate morphology of studied materials. The instrument was equipped with a dual-EELS system Quantum ER from Gatan and Centurio EDXS system with 100 mm² SDD detector. For TEM studies, a drop of an ethanol diluted sample suspension was placed on a lacey-carbon coated nickel grid and dried at room temperature. Beside conventional TEM and high-resolution TEM (HRTEM), two observation techniques were also used in the STEM mode; high-angle annular dark-field (HAADF) imaging and bright-field (BF) imaging. The specific surface area of the powders was determined through the measurement of nitrogen adsorption-desorption isotherms by a Tristar 3000, Micromeritics (USA) instrument. The measurements were performed at -196 °C (77 K). The samples were outgassed under vacuum for 16 h at 110 °C (383 K). The mass of the samples in the analyser was $\approx$ 0.1 g. The specific surface area was calculated from the adsorption measurements in the relative pressure (p/p_0) range of 0.05–0.25. Pore size distribution was calculated using the Barrett, Joyner, and Halenda (BJH) method. The surface charge properties of the prepared samples and mean particle size were analyzed by a Zetasizer (Malvern, UK) instrument. X-ray photoelectron spectroscopy (XPS) measurements were conducted using a Versa Probe 3 AD (PHI, Chanhassen, USA) equipped with a monochromatic Al K α X-ray source. The source operated at an accelerating voltage of 15 kV, and 46 W. Powder samples were mounted on double-sided Scotch tape and positioned at the center of the XPS holder. Spectra were acquired for each sample over a 200 $\times$ 200 μ m analysis area, with the charge neutralizer activated during data collection. Survey spectra were measured using a pass energy of 224 eV and a step size of 0.2 eV. High-resolution (HR) spectra were recorded with a pass energy of 27 eV and a step size of 0.05 eV. To ensure high-quality spectral data with a good signal-to-noise ratio, at least 10 sweeps were performed for each measurement. The energy scale of the XPS spectra and any possible charging effects were corrected by referencing the C=C peak in the C 1s spectrum with a binding energy (BE) of 284.8 eV. Spectral quantification was carried out using MultiPak 9.9.1 software with Shirley background correction. Deconvolution (Fitting) was performed using

CasaXPS 2.3.26 software, with a Shirley type background and 75 – 25 % Gaussian–Lorentzian peak shapes. Raman Spectroscopy was performed with Bravo Handheld Raman Spectrometer, Bruker Optic. Fourier-Transform Infrared Spectroscopy (FTIR) was used to record infrared spectra between 4000 cm^{-1} and 400 cm^{-1} using a Bruker Alpha-II (FT-IR spectrophotometer with ATR module)

RESULTS

Optoelectronic properties

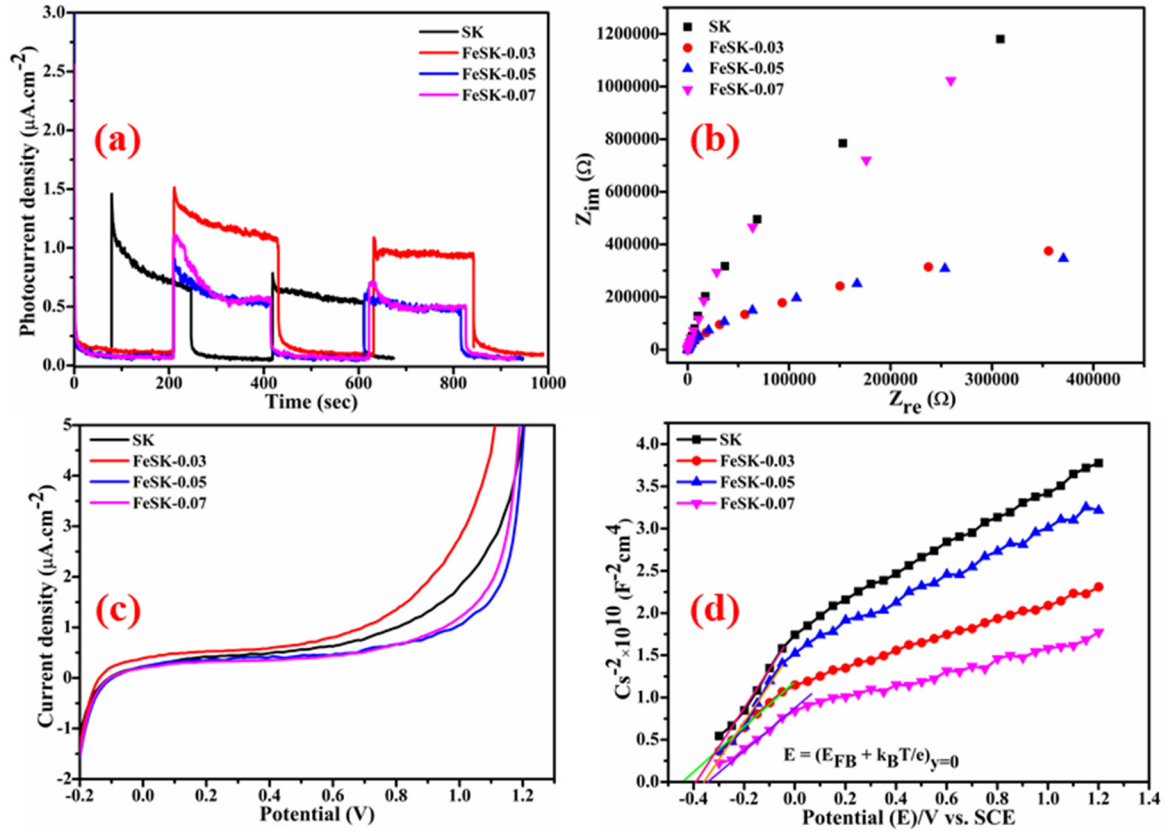


Figure 1. PEC results of pure SrTiO₃ and Fe doped SrTiO₃ (a) transient photocurrent response, (b) Nyquist plot, (c) linear sweep voltammograms, and (d) Mott–Schottky

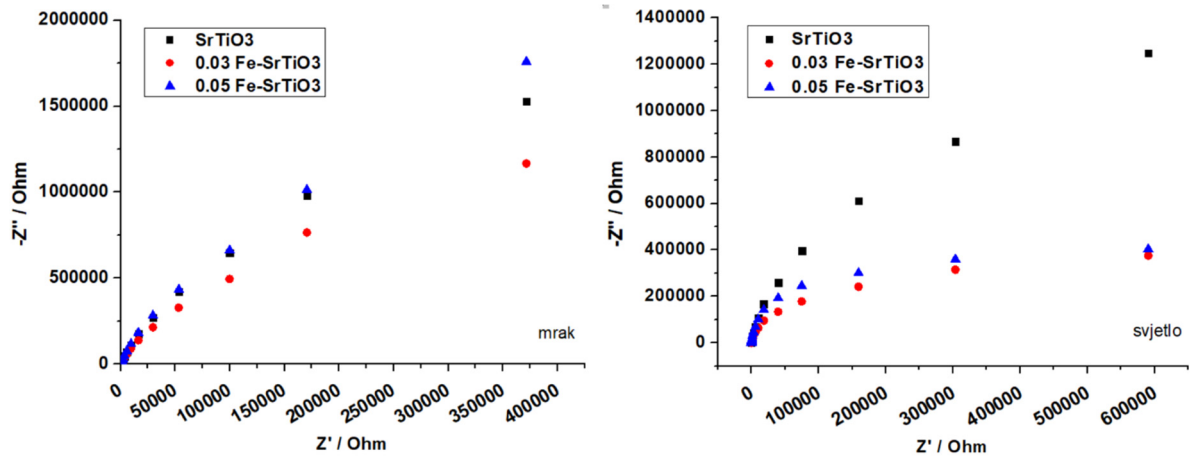


Figure 2. EIS-light vs dark for pure SrTiO₃ and Fe doped SrTiO₃

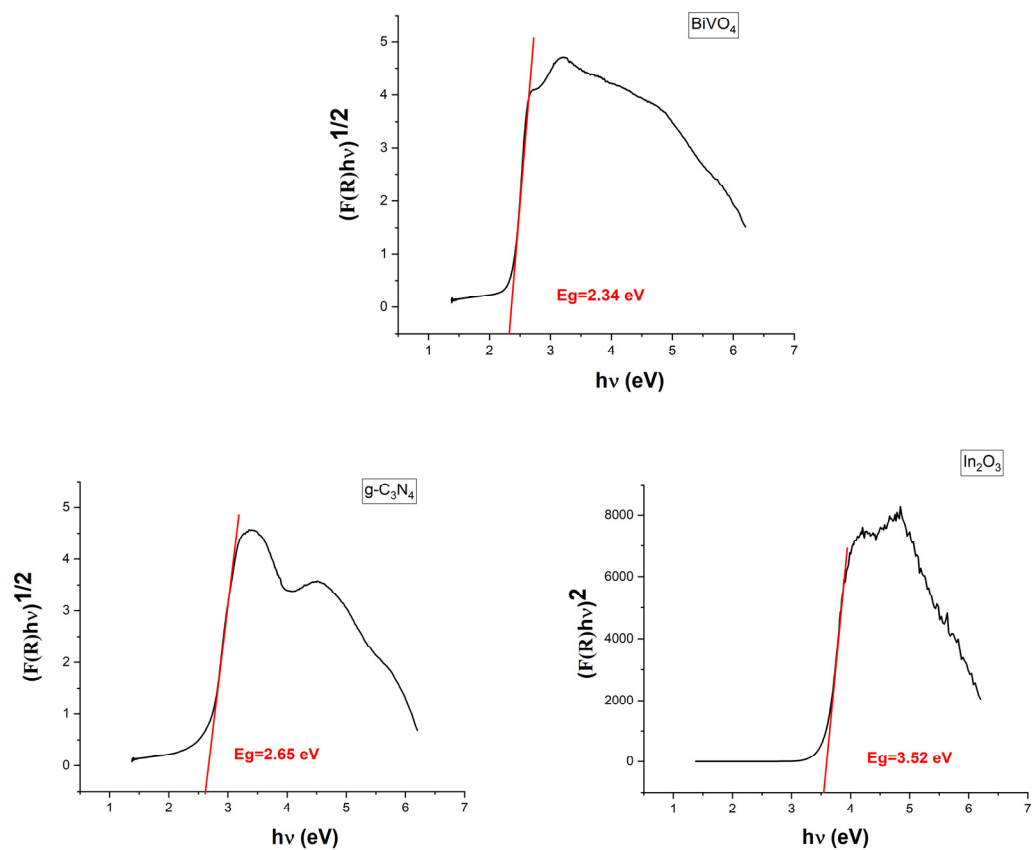


Figure 3. Tauc plots: (a) indirect band gap of BiVO_4 (b) indirect band gap of $\text{g-C}_3\text{N}_4$ (c) direct band gap of In_2O_3

Table 1. Band gaps of photocatalysts determined from Tauc plots

Material	BiVO_4	$\text{g-C}_3\text{N}_4$	In_2O_3
Band gap (eV)	2.34	2.65	3.52

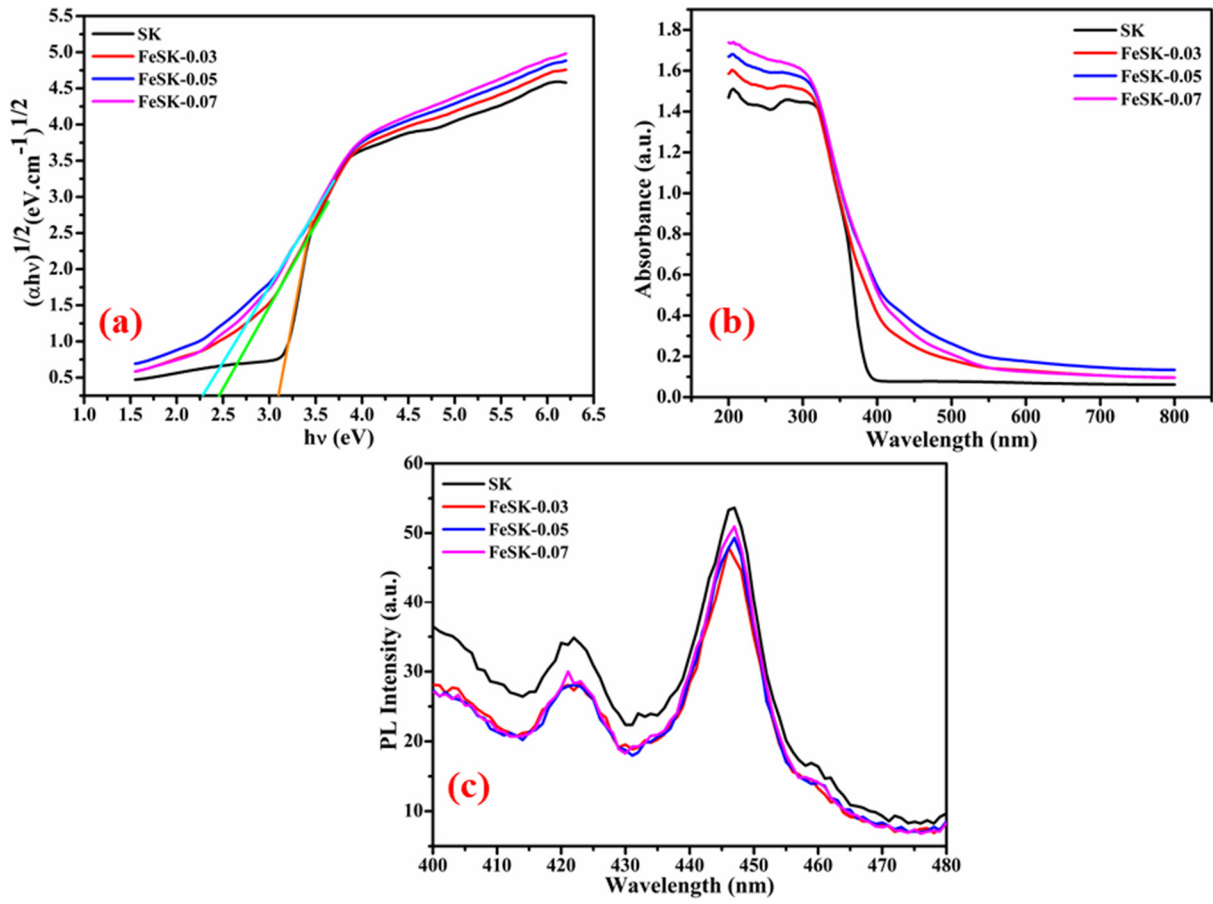


Figure 4. (a) UV-Visible absorbance spectra, (b) Tauc plot, and (c) Photoluminescence (PL)

spectra of pure SrTiO₃ and Fe doped SrTiO₃ samples

Surface, structural and morphology properties

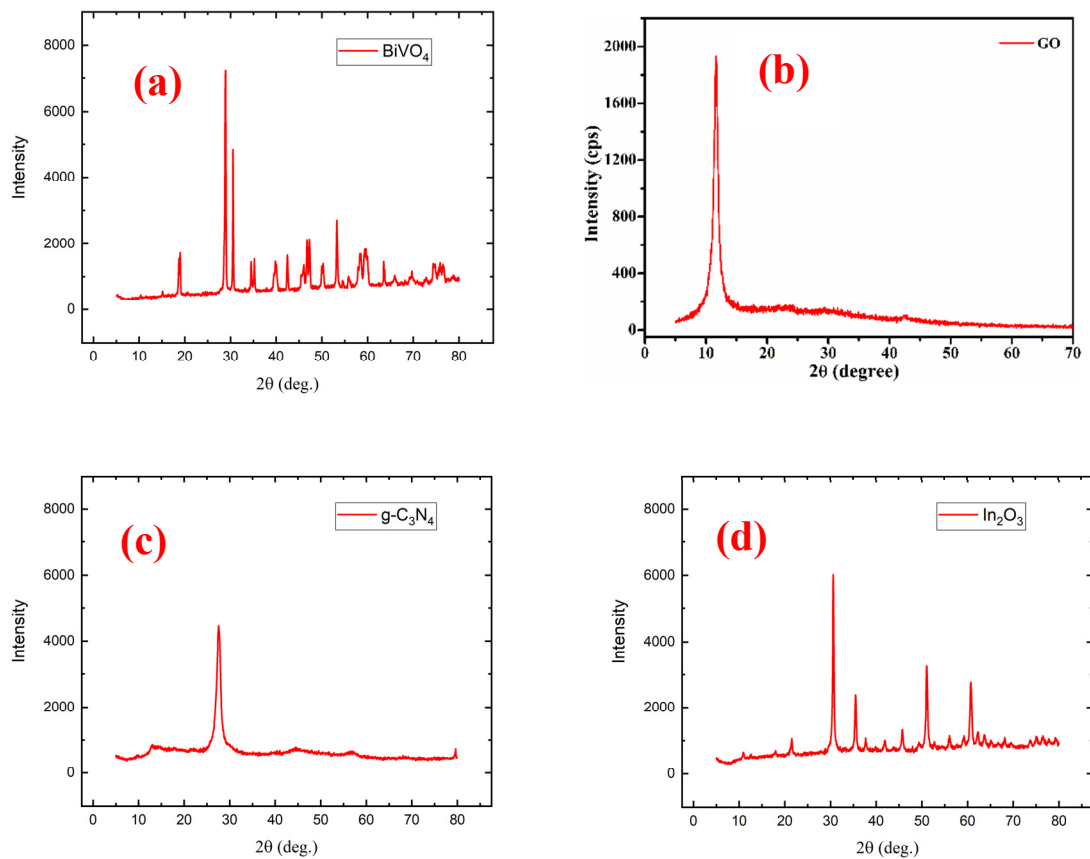


Figure 5. XRD patterns of (a) BiVO_4 (b) GO (c) $\text{g-C}_3\text{N}_4$ (d) In_2O_3

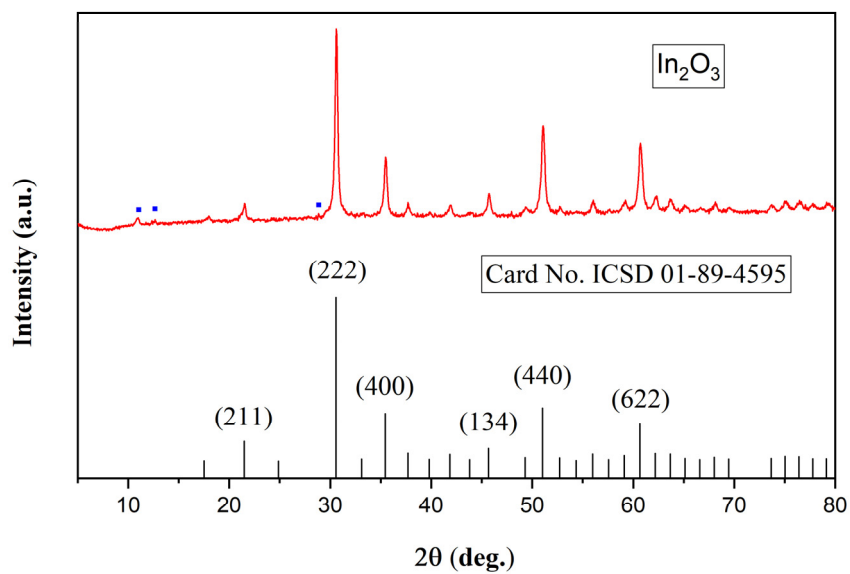


Figure 6. XRD pattern of In_2O_3 and the standard ICSD card no. 01-89-4595

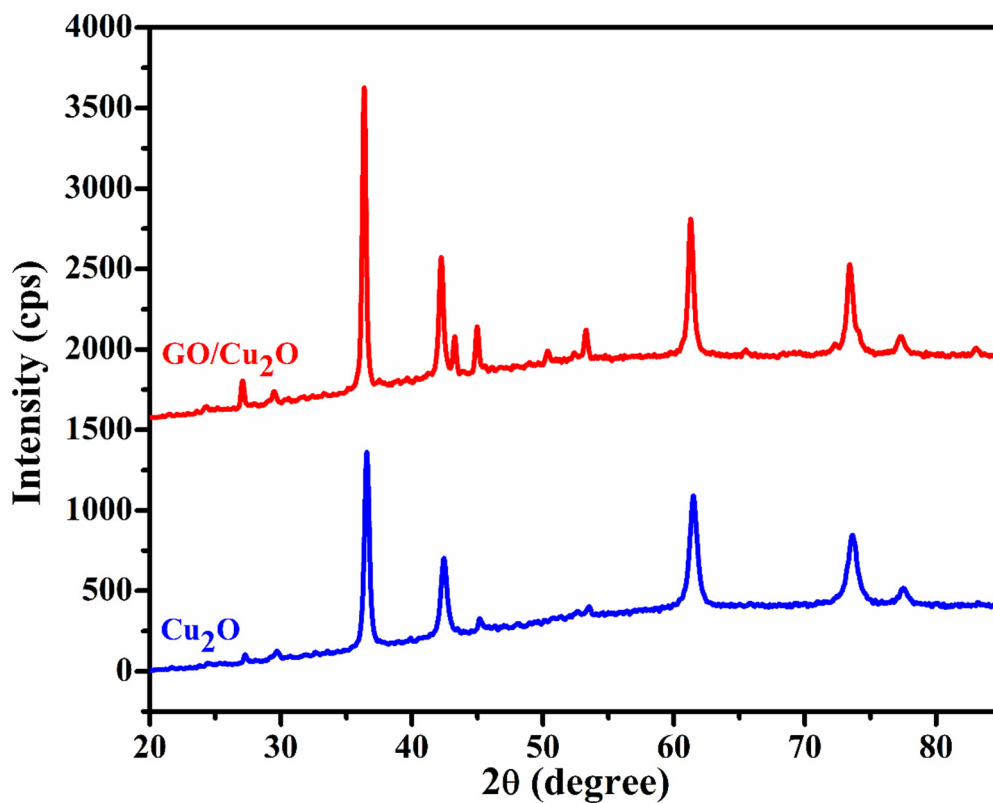


Figure 7. XRD pattern of Cu_2O and $\text{GO/Cu}_2\text{O}$

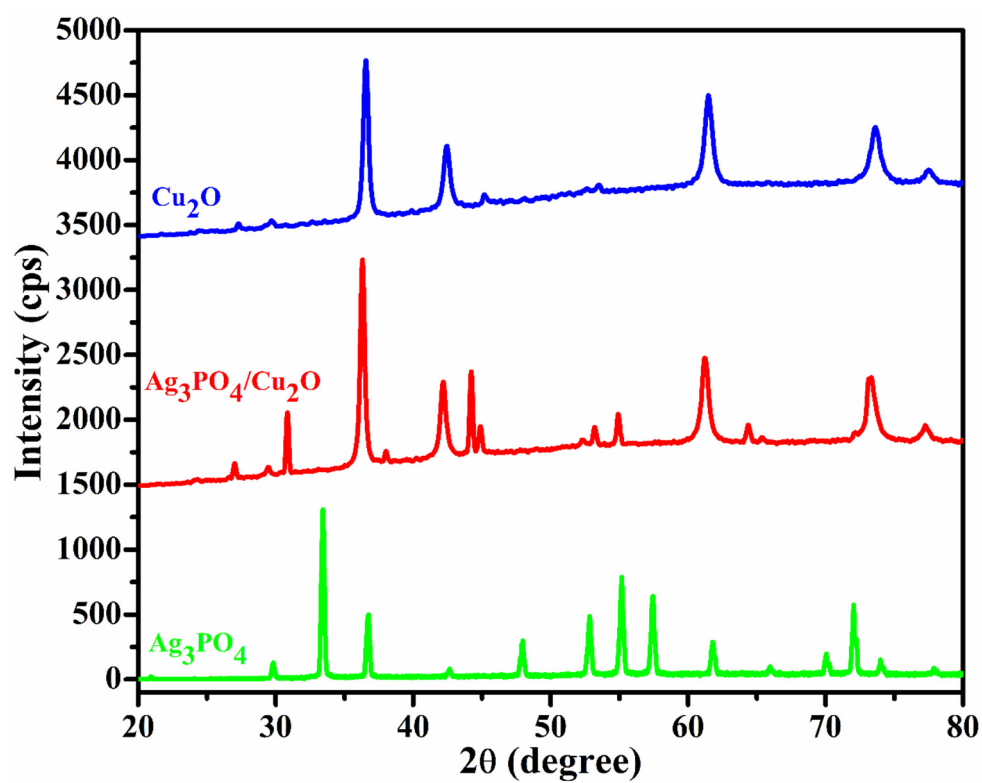


Figure 8. XRD pattern of Ag_3PO_4 , Cu_2O and $\text{Ag}_3\text{PO}_4/\text{Cu}_2\text{O}$ samples

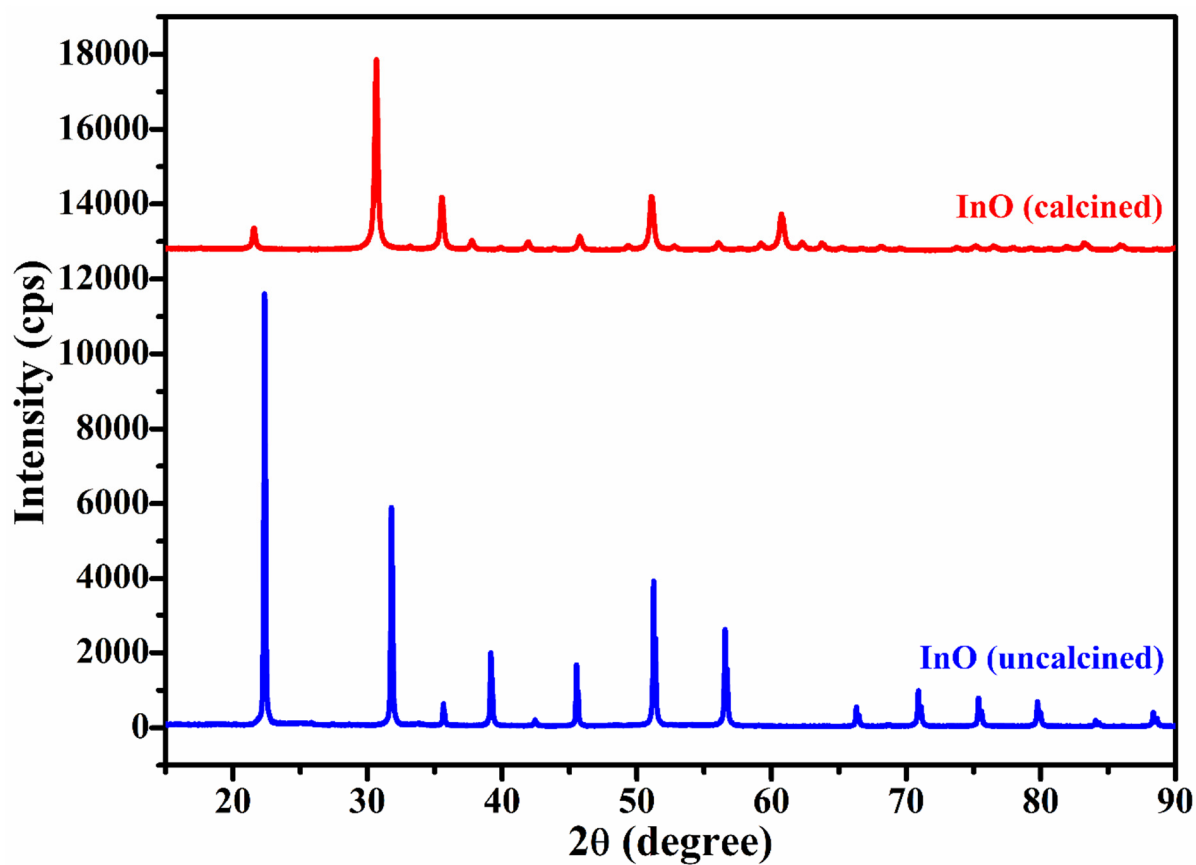


Figure 9. XRD pattern of In_2O_3 (uncalcined) and In_2O_3 (Calcined)

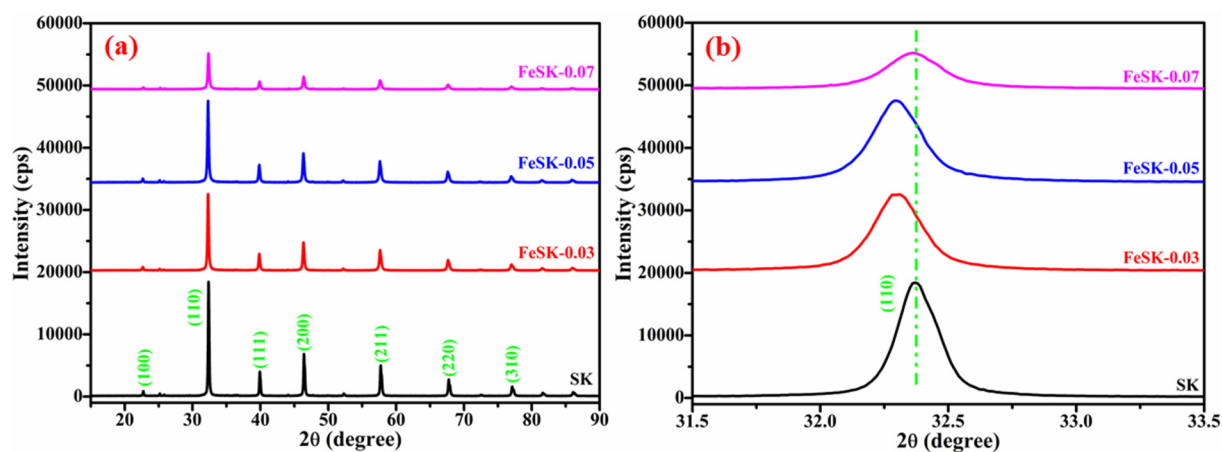


Figure 10. XRD Pattern of (a) SrTiO_3 and Fe doped SrTiO_3 (b) Zoomed view of the most intense (110) peak

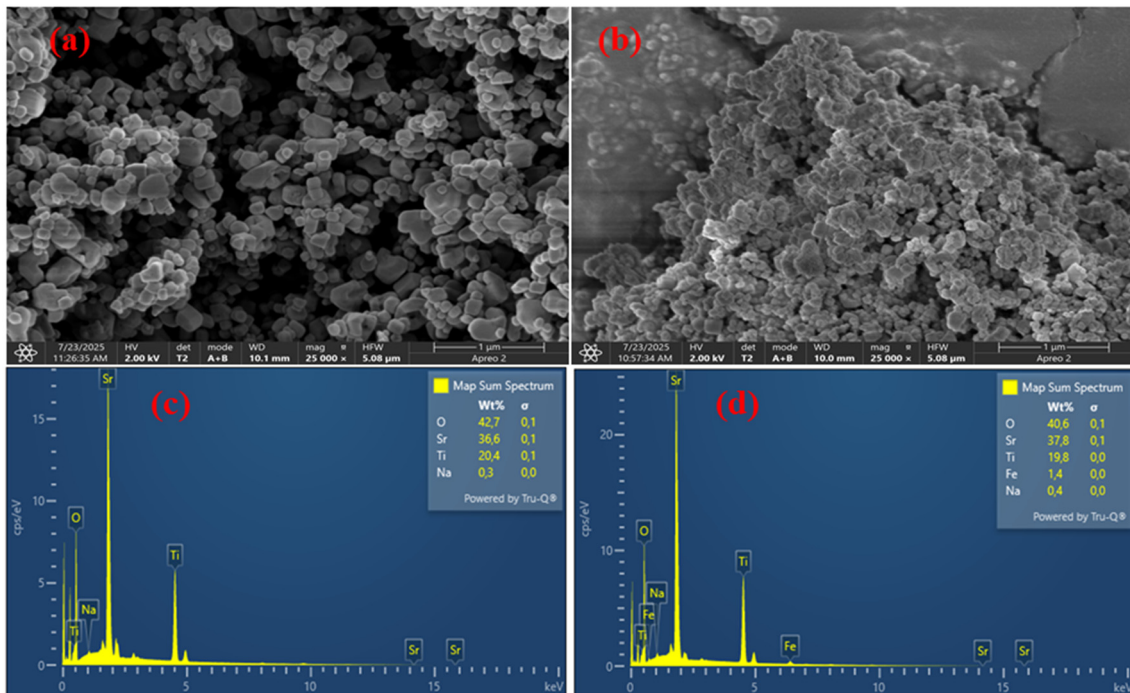


Figure 11. (a,b) SEM images of SK and FeSK-0.03, and (c,d) corresponding EDS spectra

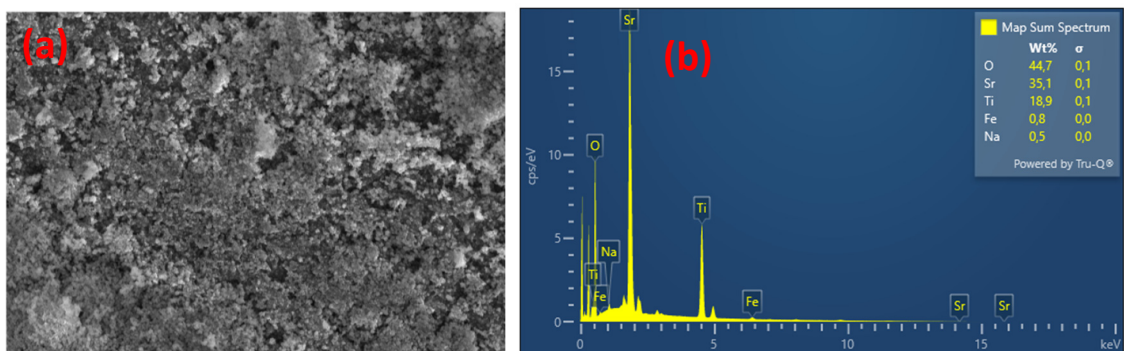


Figure 12. (a) SEM images of FeSK-0.05 and (b) corresponding EDS spectra

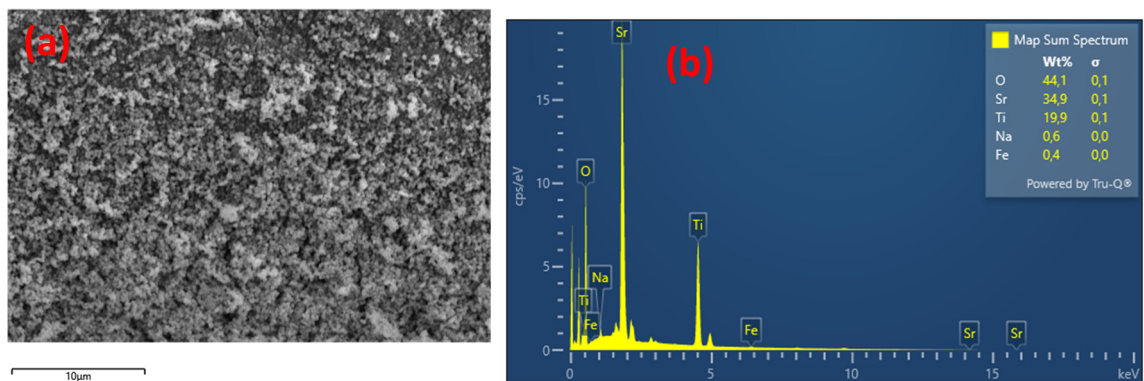


Figure 13. (a) SEM images of FeSK-0.07 and (b) corresponding EDS spectra

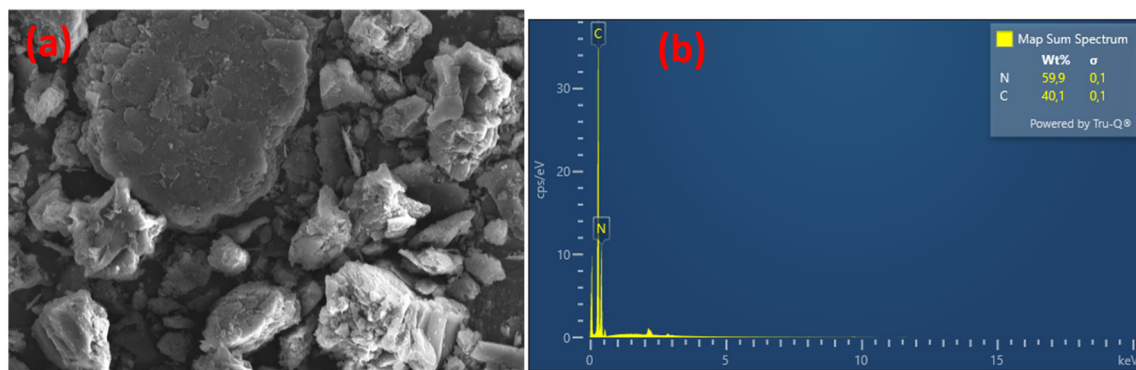


Figure 14. (a) SEM images of g-C₃N₄ and (b) corresponding EDS spectra

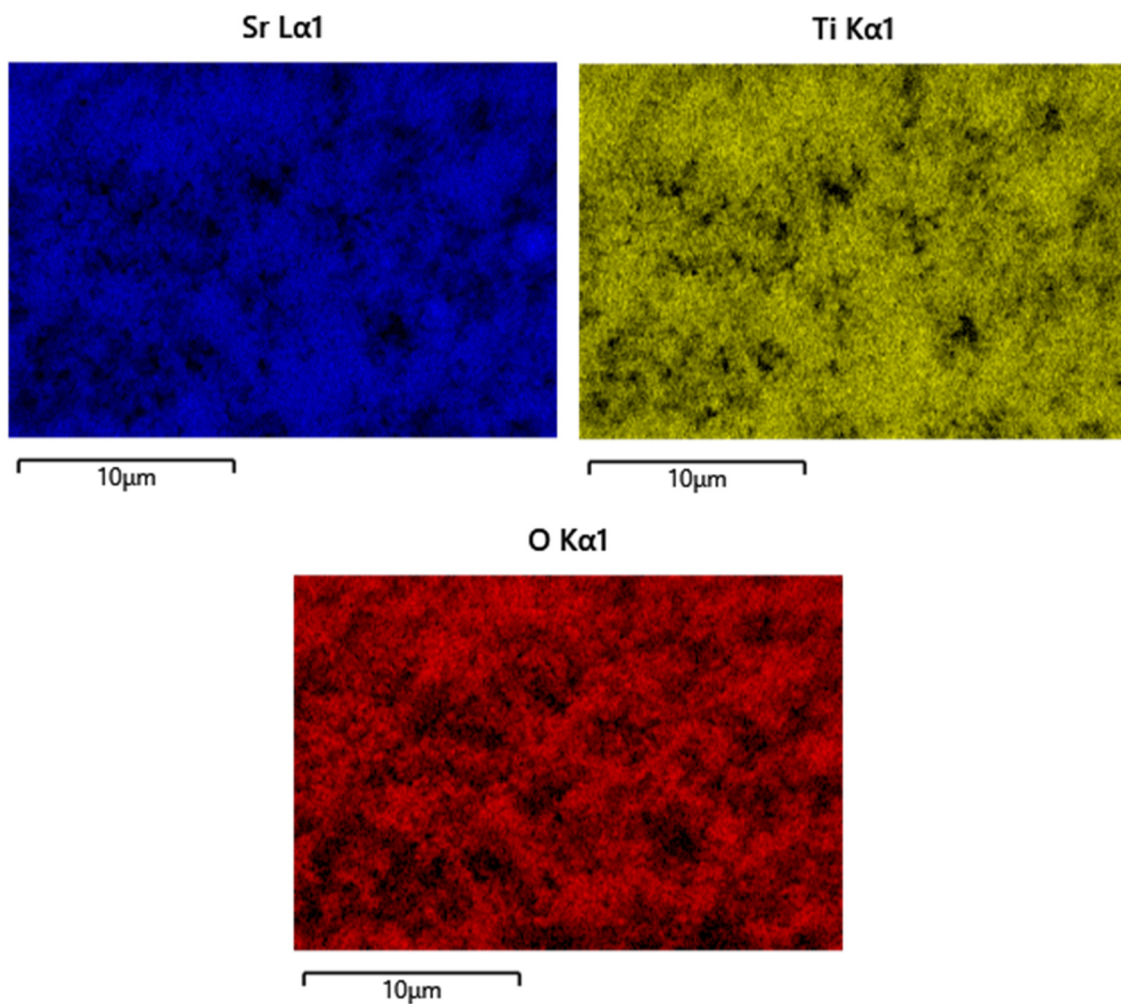


Figure 15. SEM–EDS elemental mapping SK (Sr, Ti, O)

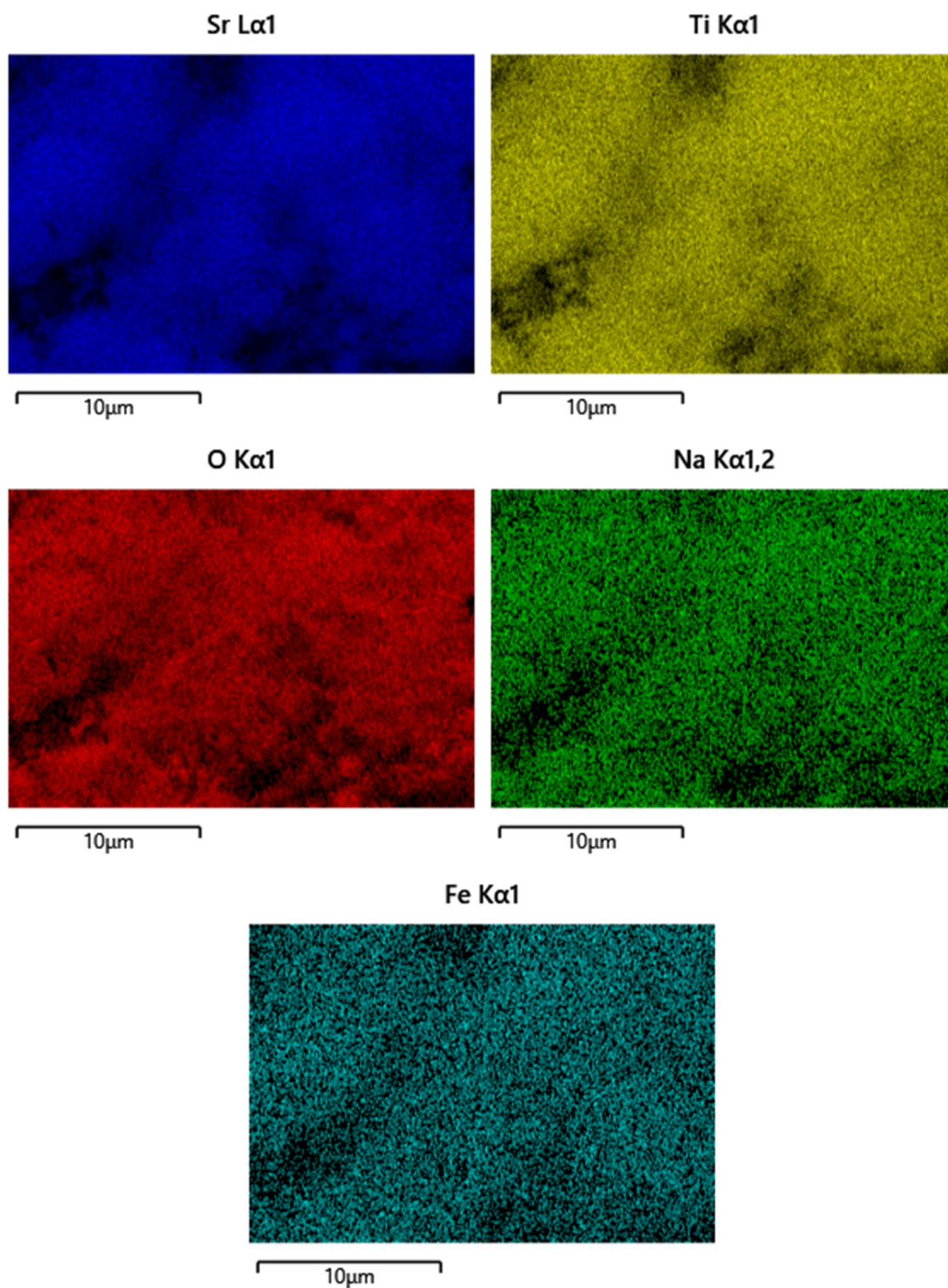


Figure 16. SEM–EDS elemental mapping of FeSK-0.03 (Sr, Ti, O, Na)

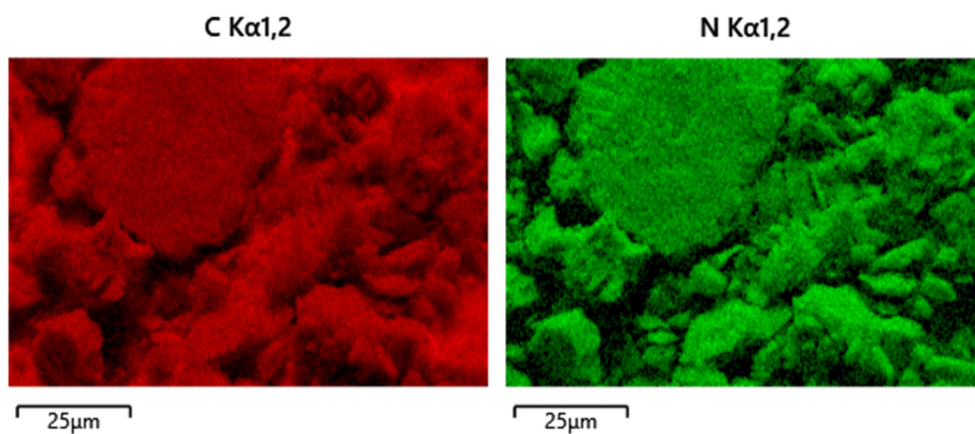


Figure 17. SEM–EDS elemental mapping of g-C₃N₄ (C, N)

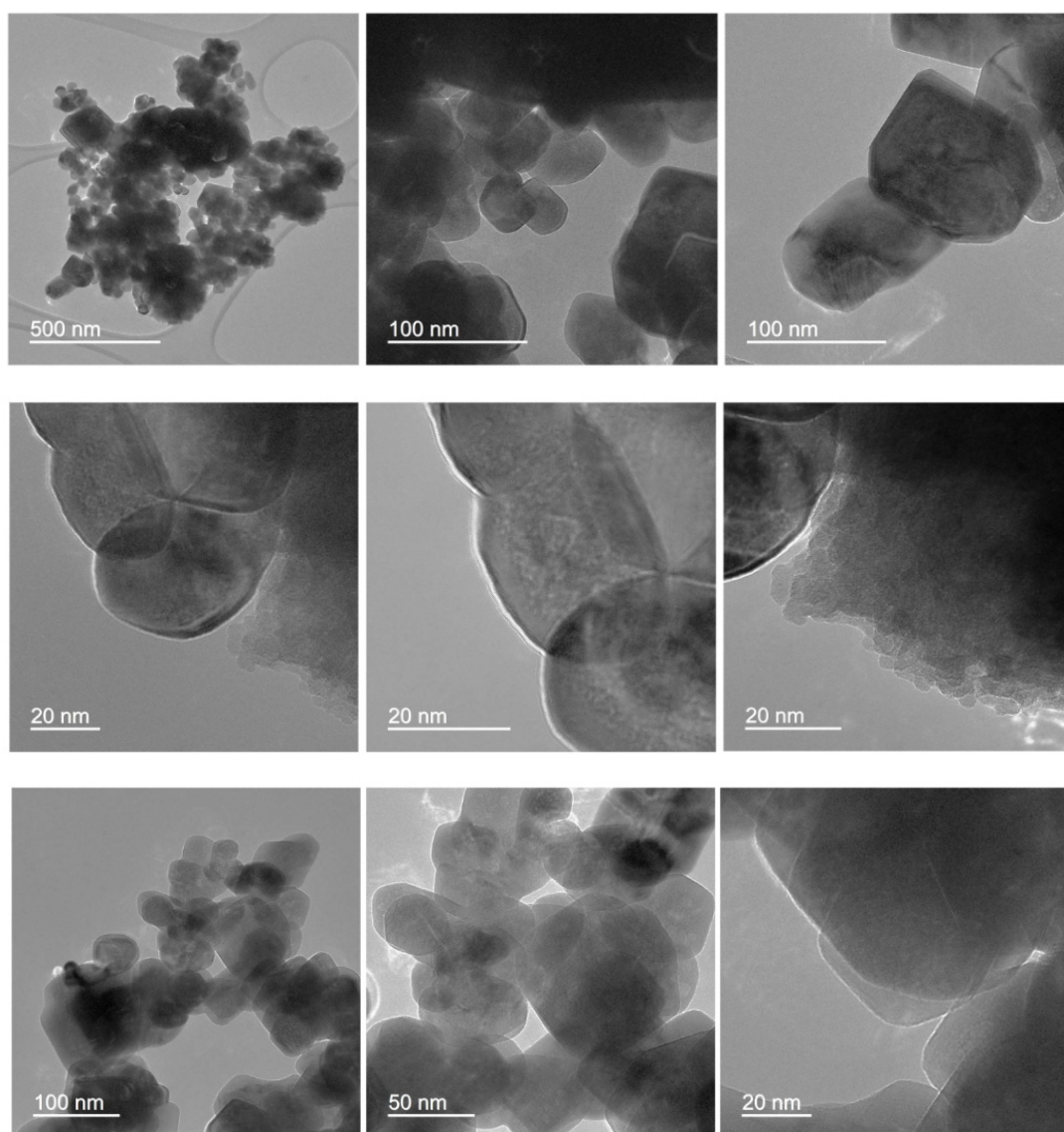


Figure 18. TEM micrographs of FeSK-0.03

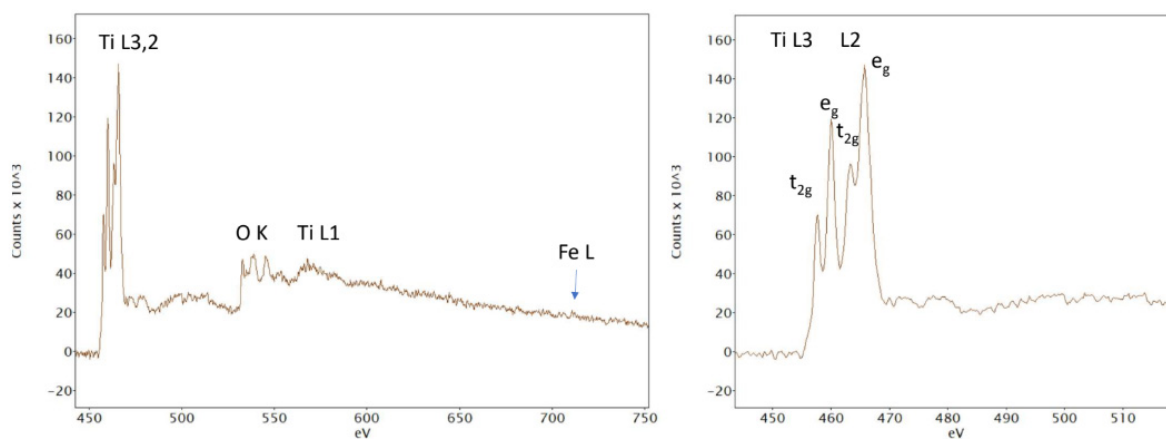


Figure 19. EELS spectrum characteristic for Ti^{4+}

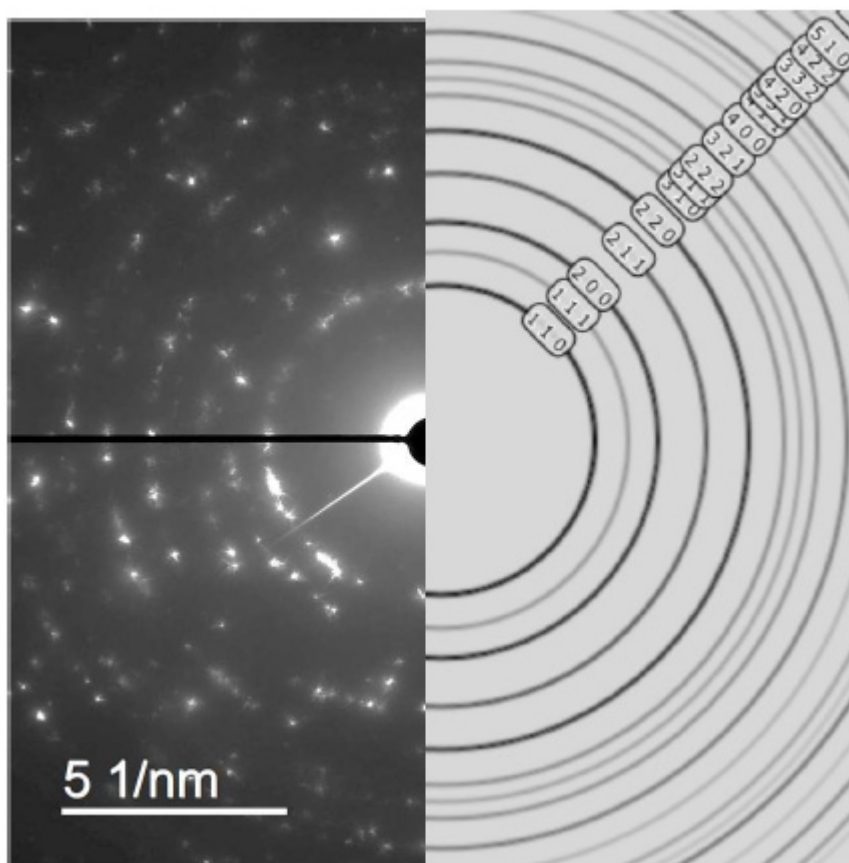


Figure 20. Experimental SAED - simulated SrTiO_3 – Pm-3m

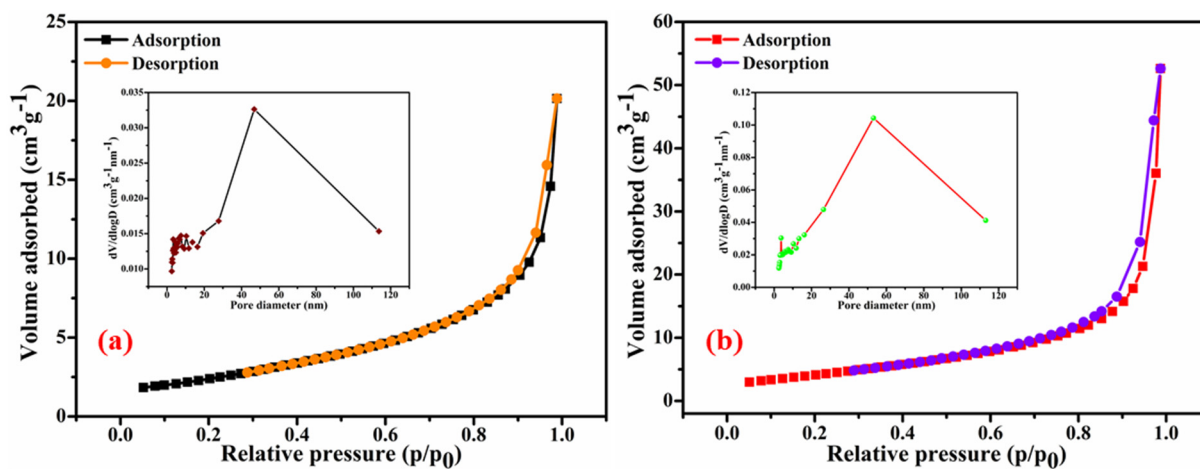


Figure 21. Nitrogen adsorption-desorption isotherm of (a) SrTiO₃ (SK), (b) FeSrTiO₃ (FeSK-0.03) samples; and their corresponding BJH plot (insets)

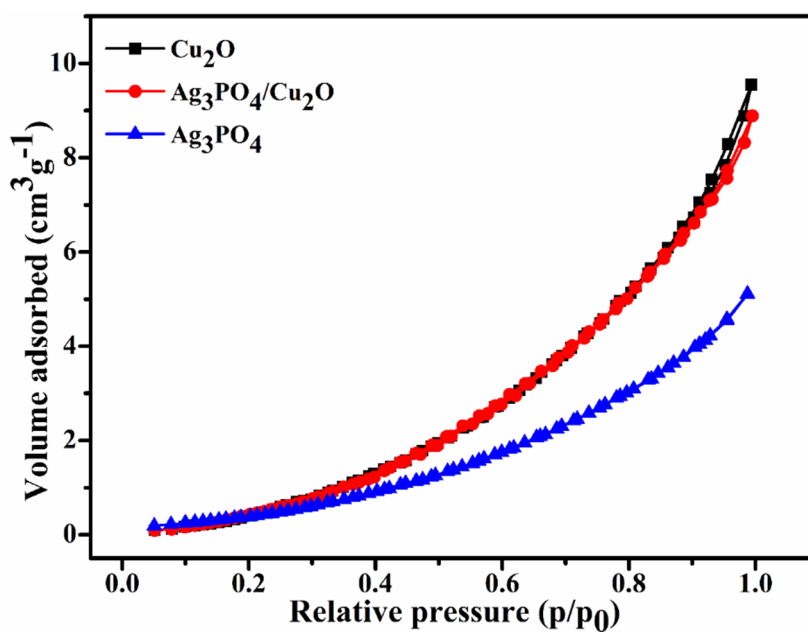


Figure 22. Nitrogen adsorption-desorption isotherms of Ag₃O₄, Cu₂O, and Ag₃PO₄/Cu₂O

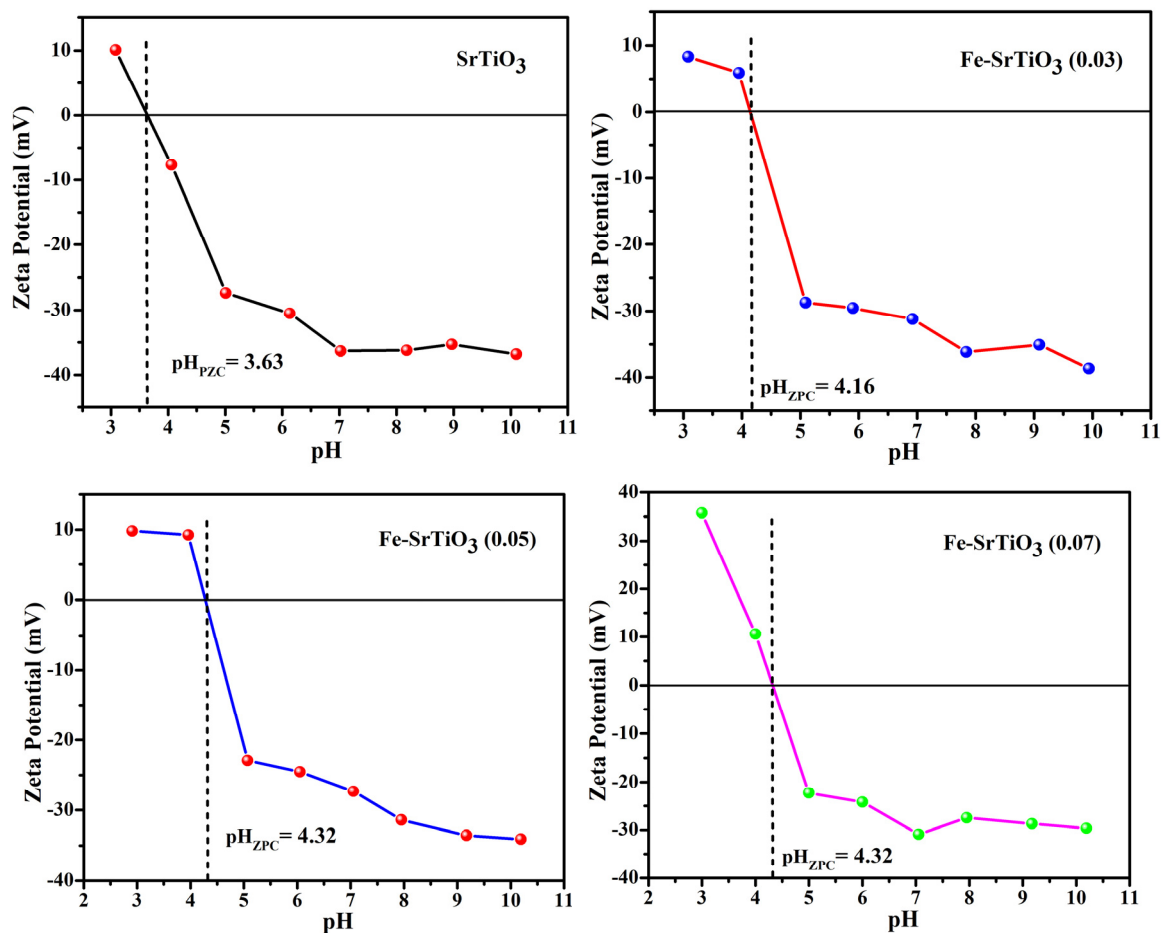


Figure 23. pH dependent zeta potential of SrTiO₃ (SK) and Fe doped SrTiO₃ (FeSK) samples

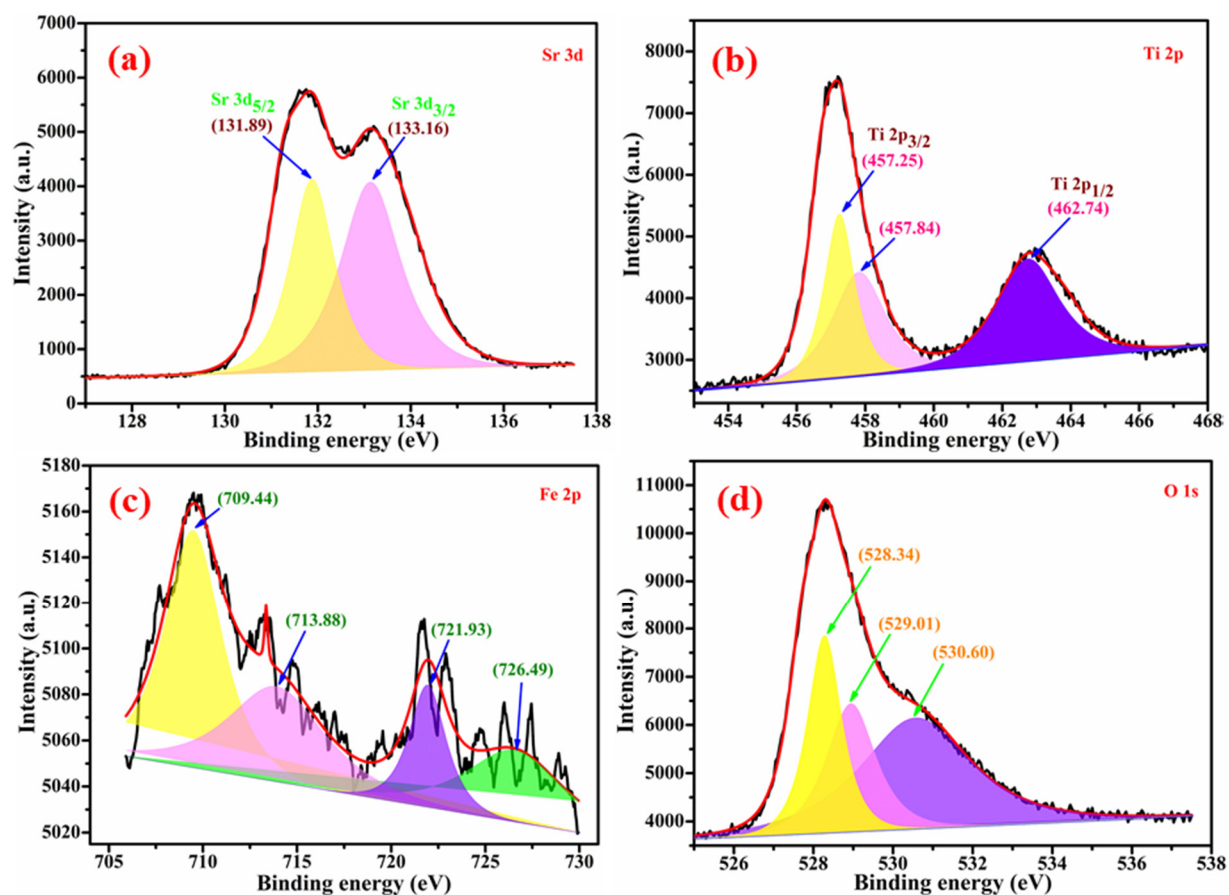
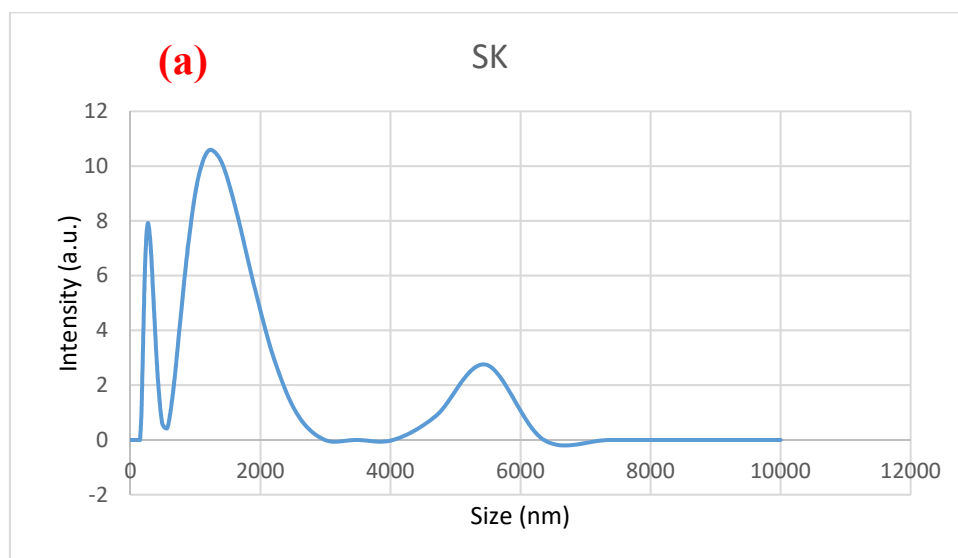


Figure 24. XPS spectra of (a) Sr 3d, (b) Ti 2p, (c) Fe 2p, and (d) O 1s for FeSK-0.03 sample



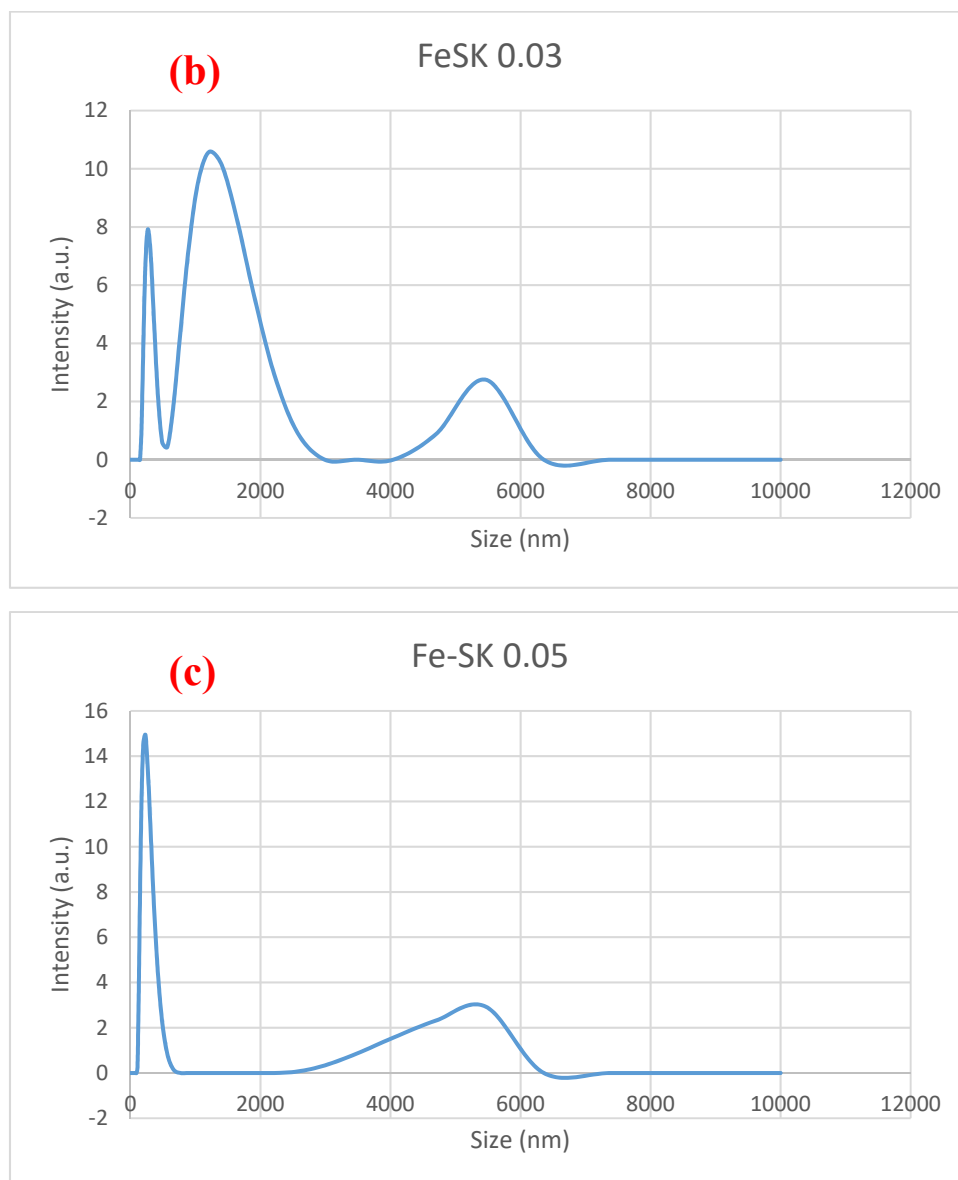


Figure 25. Particle size distribution of SrTiO_3 (a) and Fe doped SrTiO_3 (b,c) samples

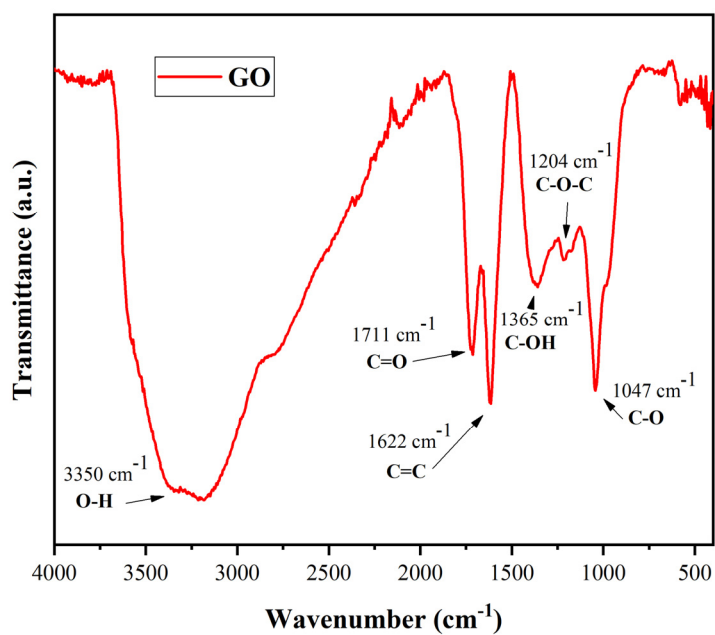


Figure 26. FTIR spectra of graphene oxide

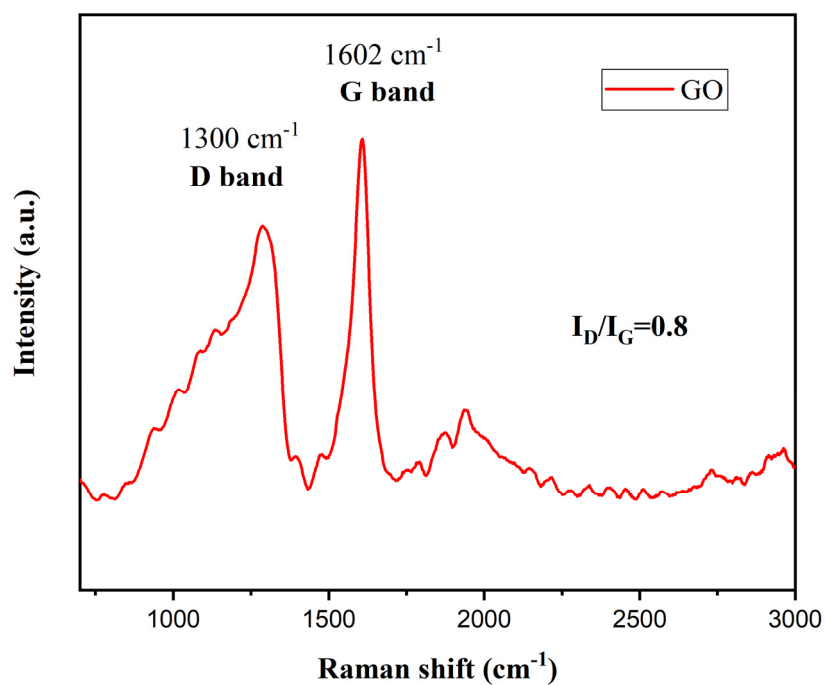


Figure 27. Raman spectra of graphene oxide

Characterization of WO₃ un-modified and modified samples

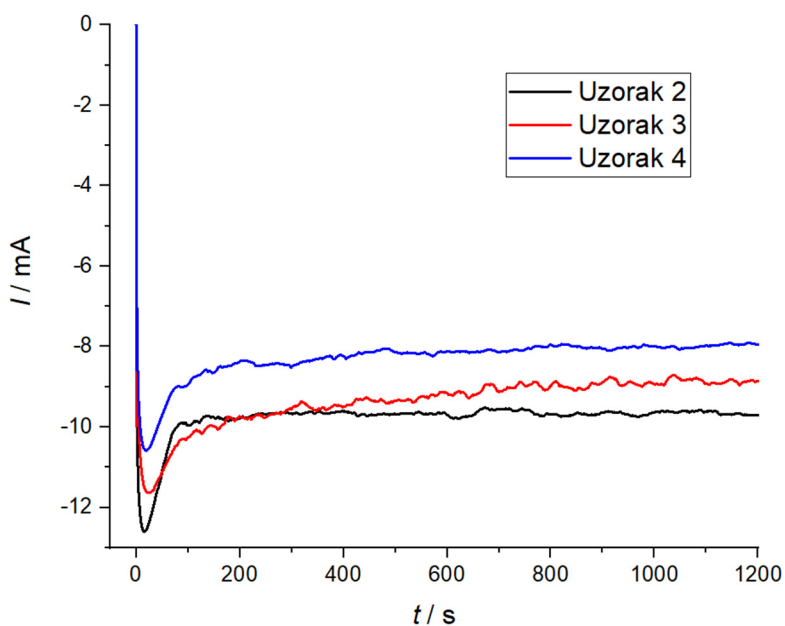


Figure 28. Graphical representation of electrodeposition of WO₃ and modified WO₃ by chronoamperometry in a three-electrode system

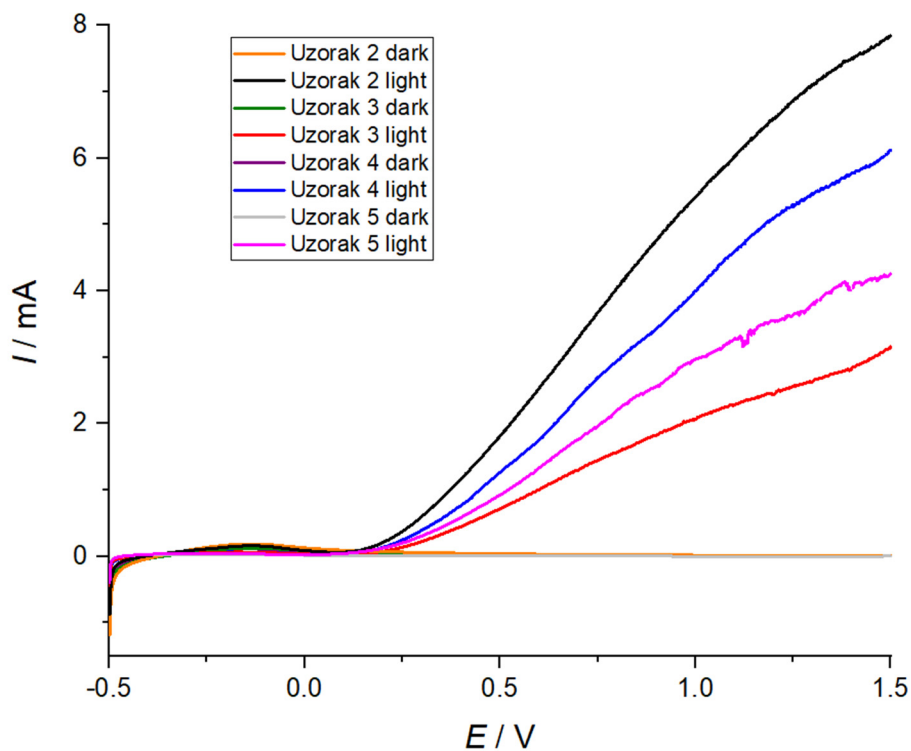


Figure 29. Graphical representation of linear polarization of illuminated and unilluminated electrodes in 0.5 M Na₂SO₄

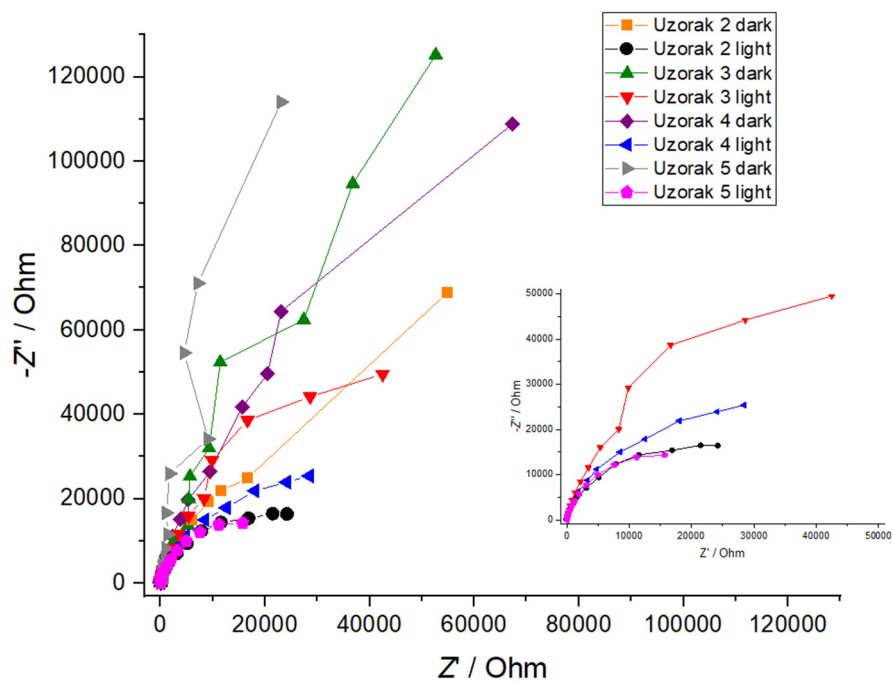


Figure 30. Graphical representation of electrochemical impedance spectroscopy response of illuminated and unilluminated electrodes in 0.5 M Na₂SO₄

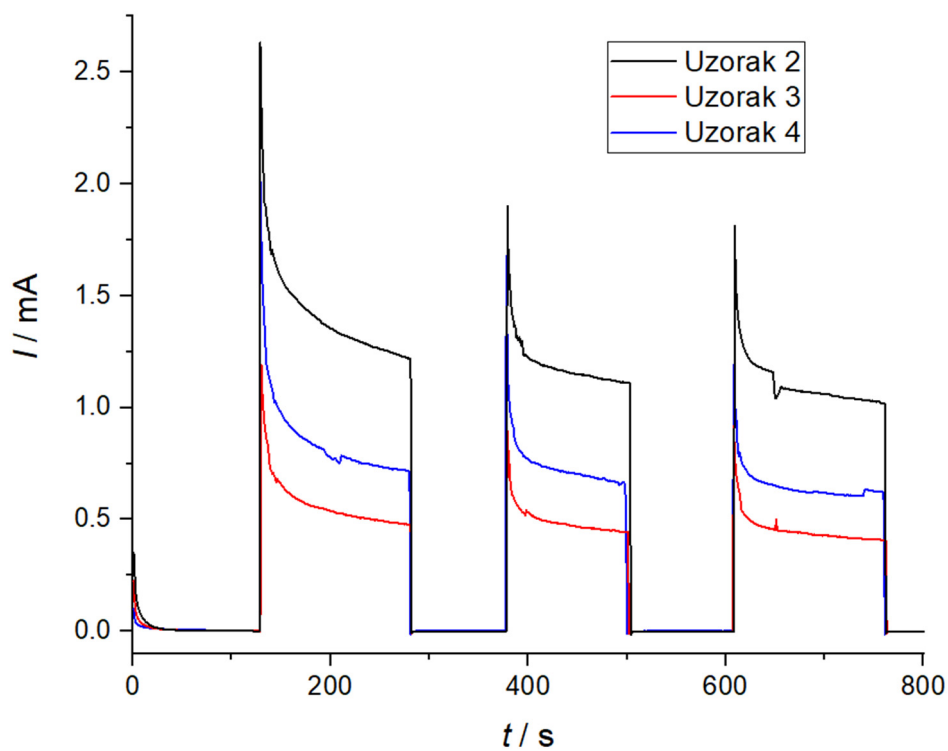


Figure 31. Graphic representation of chronoamperometry response of electrodes in 0.5 M Na₂SO₄ at 0.5 V

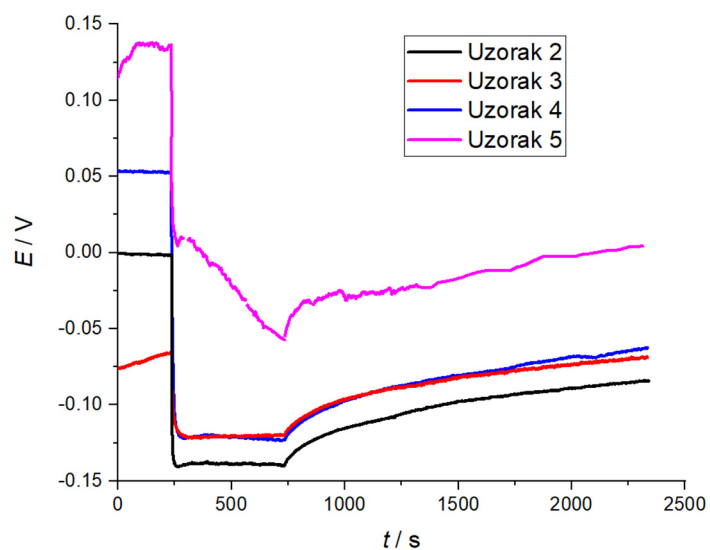


Figure 32. Graphical representation of the dependence of the open circuit potential on time with periodic exposure of the electrodes to light and darkness

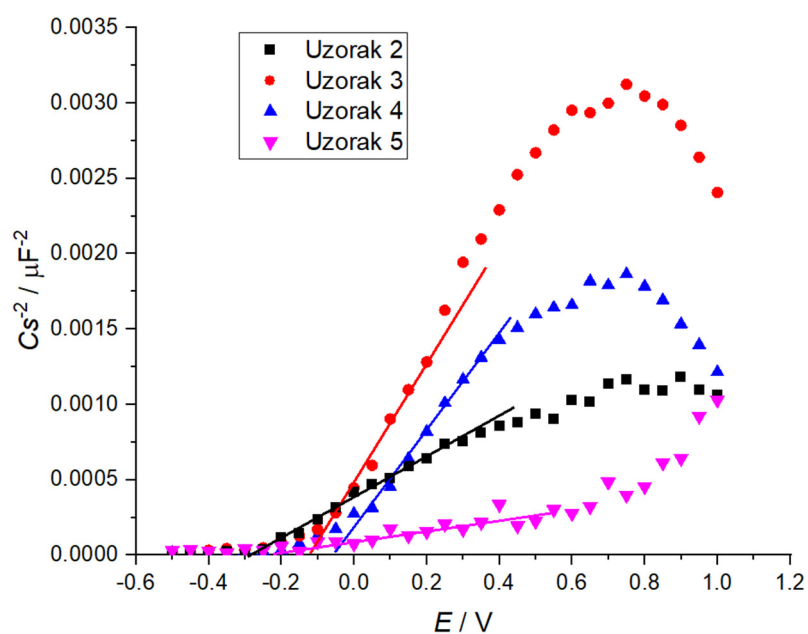
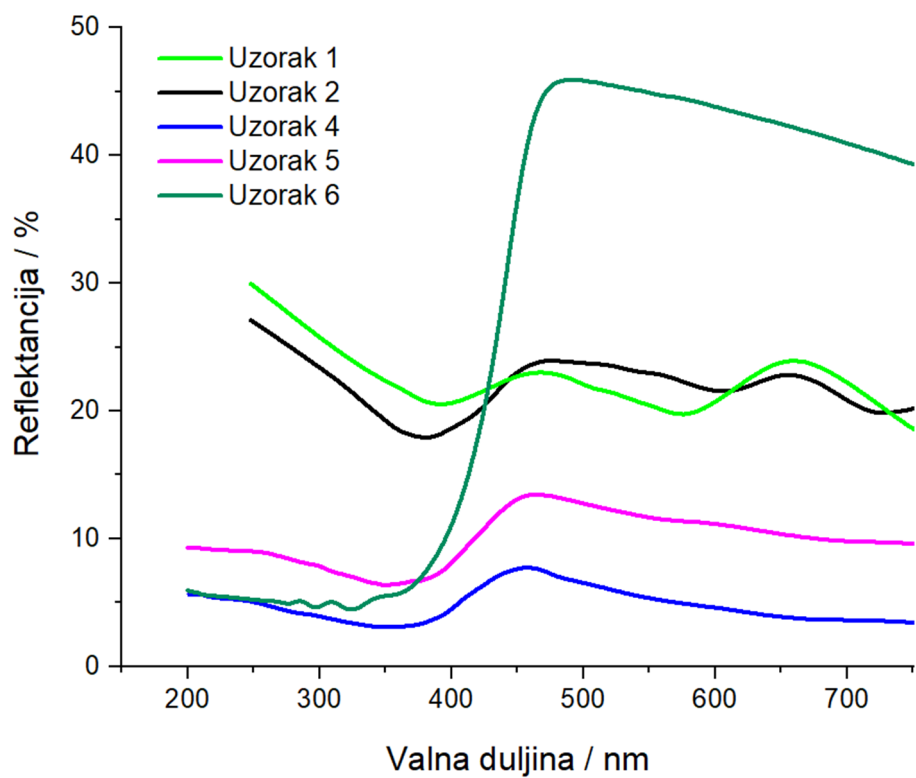


Figure 33. Mott – Schottky analysis



Slika 34. UV/Vis spectroscopy

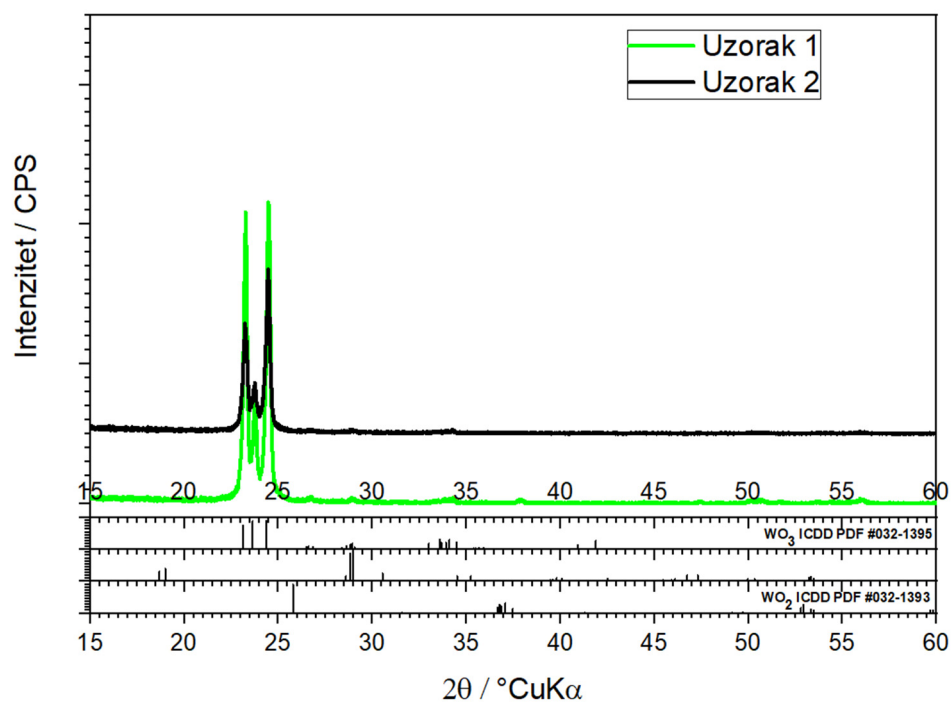


Figure 35. XRD of sample 1 i 2

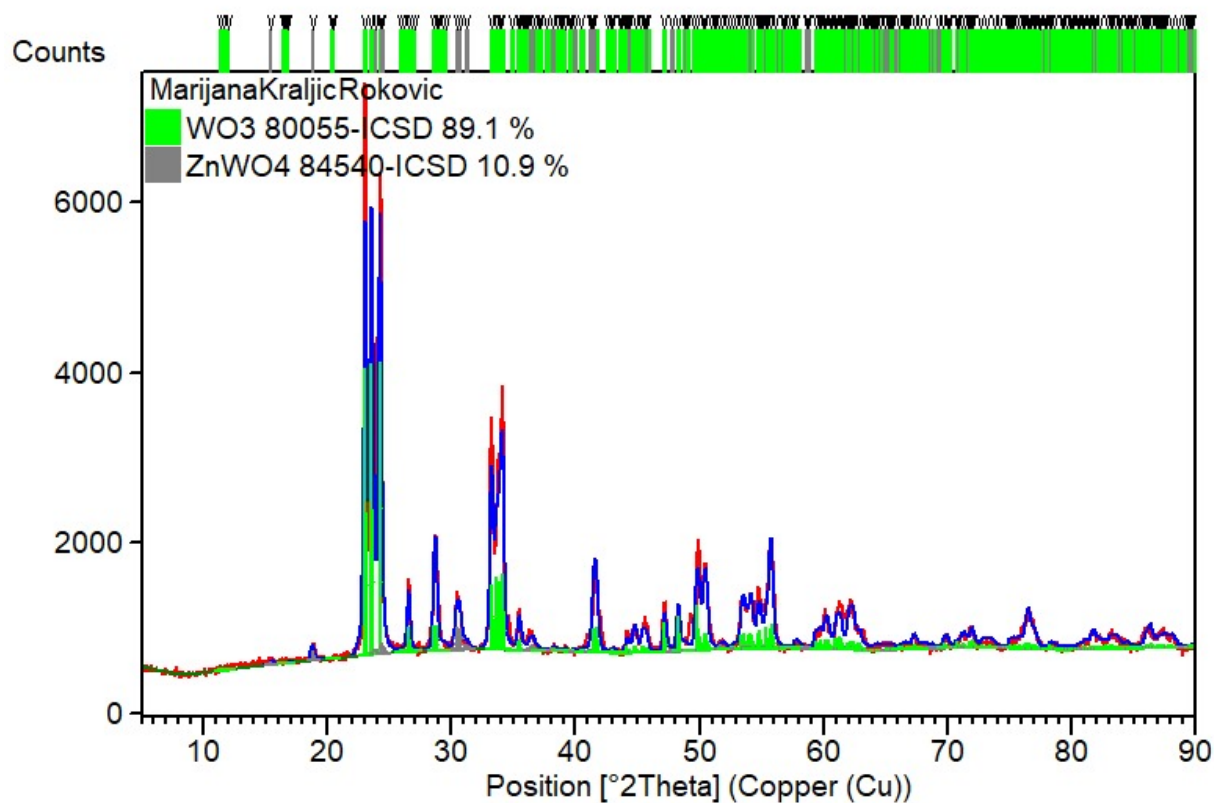
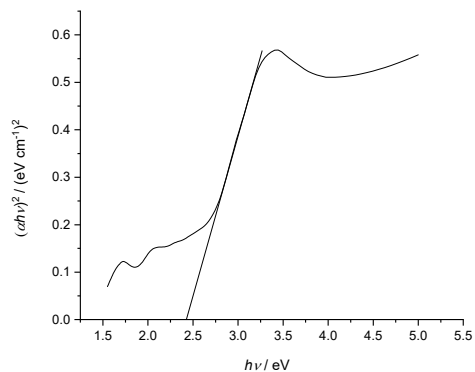


Figure 36. XRD of sample 5

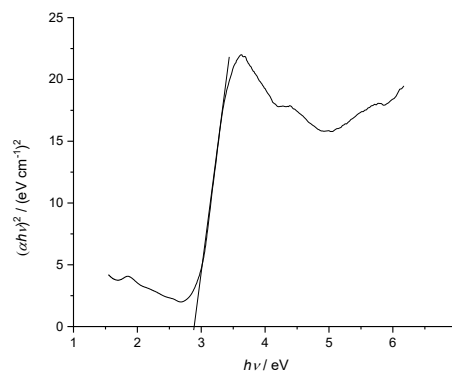
Table X. Flat band potentials

Electrode	E_{fb} / V vs SCE	E_{fb} / V vs SHE
Sample 2	-0.316	0.039
Sample 3	-0.147	0.456
Sample 4	-0.078	0.525
Sample 5	-0.250	0.105

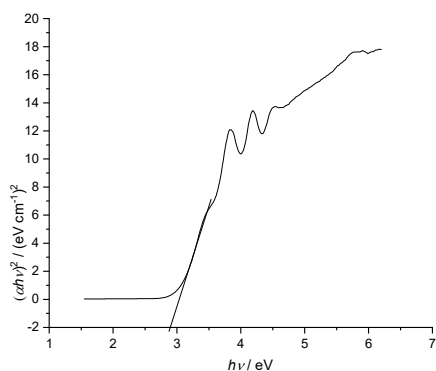
a) sample 2



b) sample 4



c) sample 5



d) sample 6

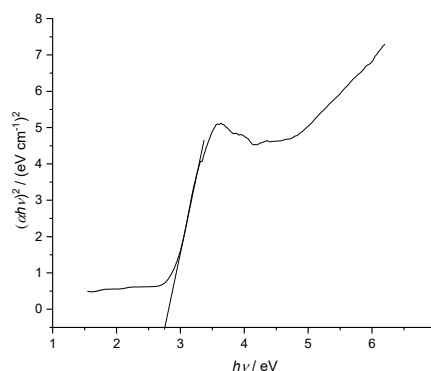


Figure 37. Tauc representation obtained by Kubelka-Munk transformation of diffuse reflectance spectra

Table 3. Band gap energy (E_g)

Electrode	E_{bg} / eV
Sample 2	2.43
Sample 4	2.89
Sample 5	2.78
Sample 6	2.77

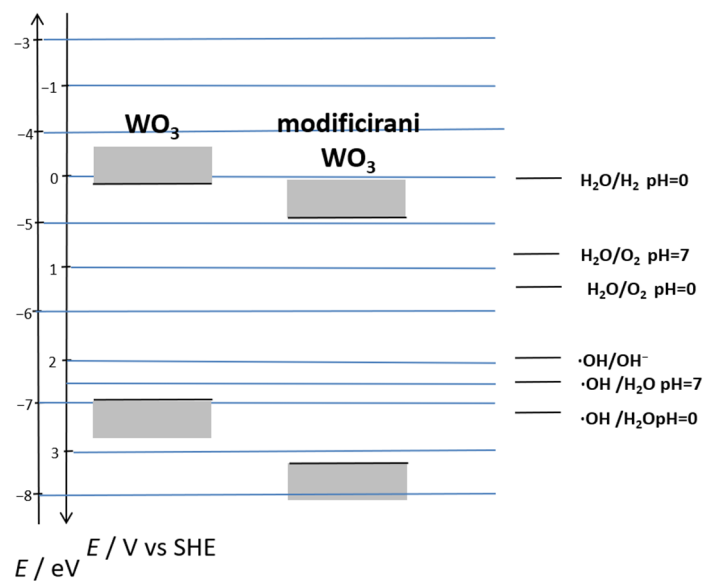


Figure 38. Energy band diagram for WO_3 (sample 2) i modified WO_3 (sample 4)

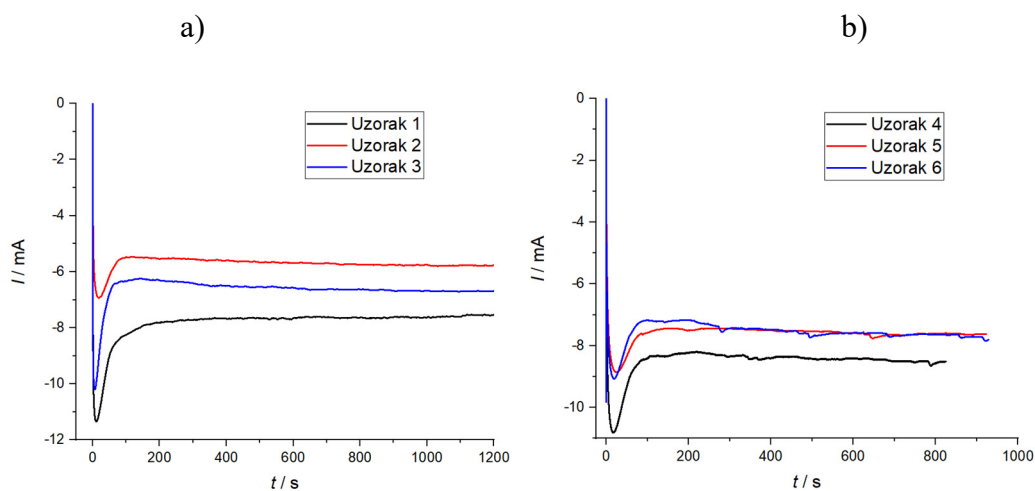


Figure 39. a) and b) Graphical representations of electrodeposition of WO_3 and modified WO_3 by chronoamperometry in a three-electrode system

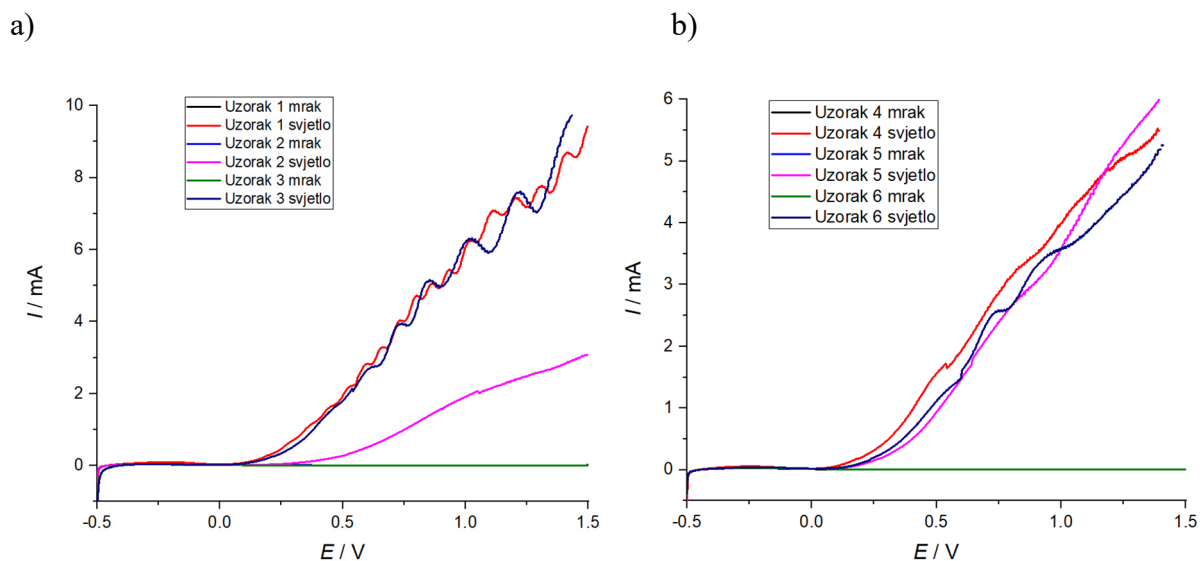


Figure 40. a) and b) Graphical representations of linear polarization of illuminated and unilluminated electrodes in 0.5 M Na_2SO_4

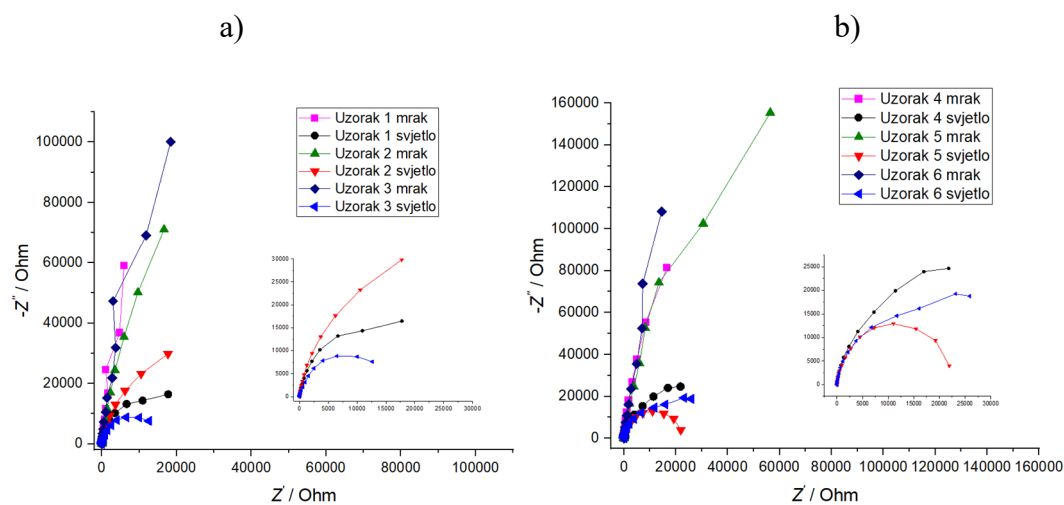


Figure 41. a) and b) Graphical representations of the Nyquist diagram for illuminated and unilluminated electrodes in 0.5 M Na_2SO_4

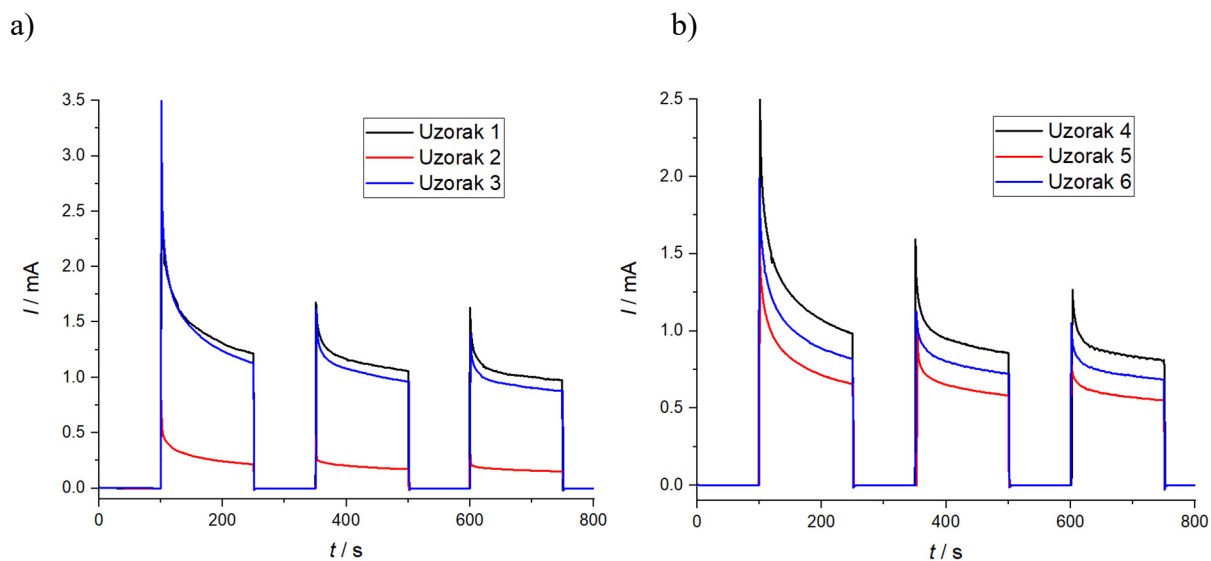


Figure 42. a) and b) Graphical representations of chronoamperometry of electrodes in 0.5 M Na_2SO_4 at 0.5 V

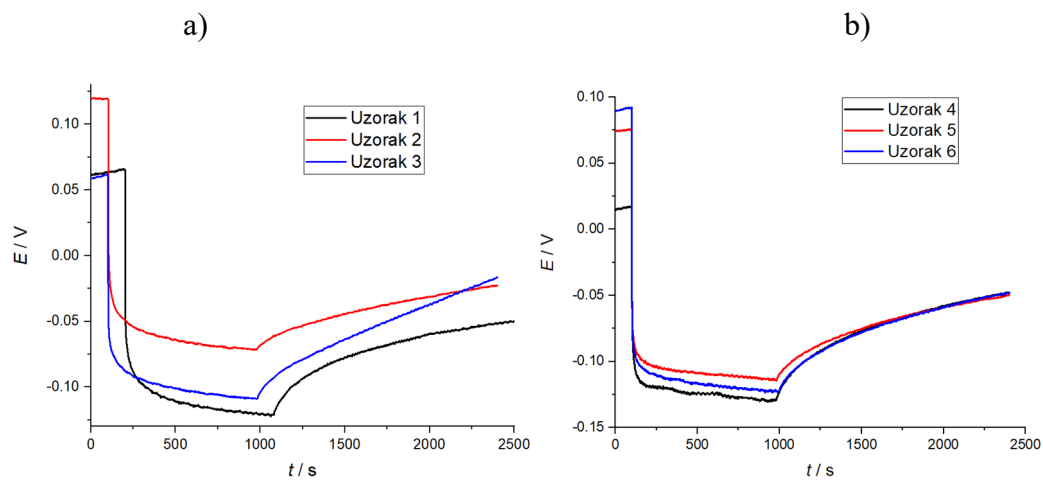


Figure 43. a) and b) Graphical representations of the dependence of the open-circuit potential on time

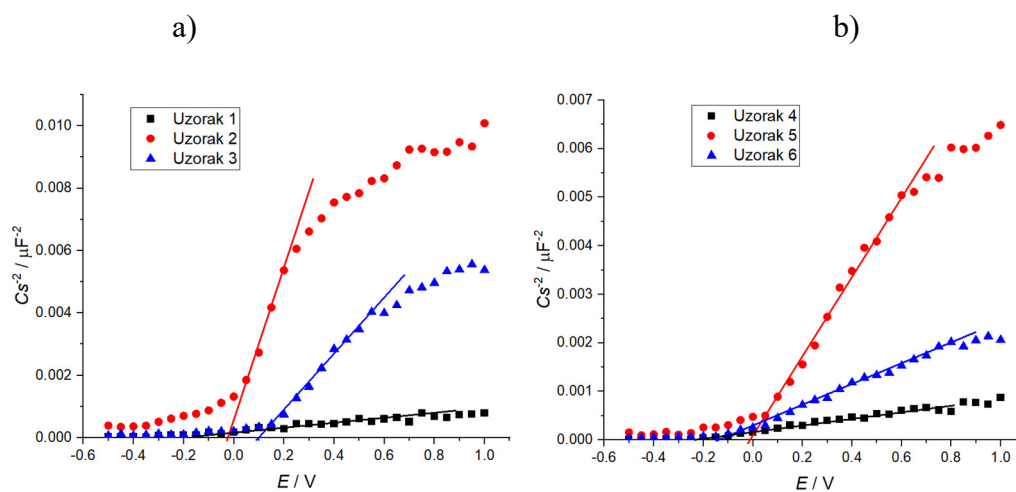


Figure 44. Mott – Schottky analysis

Tablica 2. Flat band potentials

Electrode	E_{fb} / V vs SCE (mjerena)	E_{fb} / V vs SHE (pH correction)
Sample 1	-0.183	0.130
Sample 2	-0.047	0.266
Sample 3	0.072	0.385
Sample 4	-0.255	0.058
Sample 5	-0.036	0.277
Sample 6	-0.165	0.148

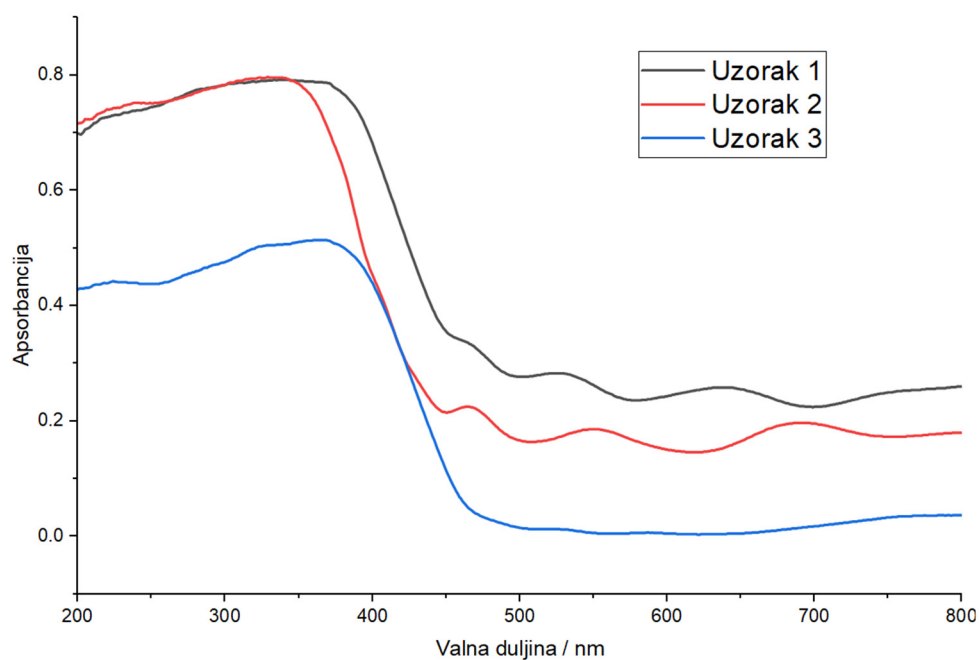


Figure 45. UV/Vis spectroscopy

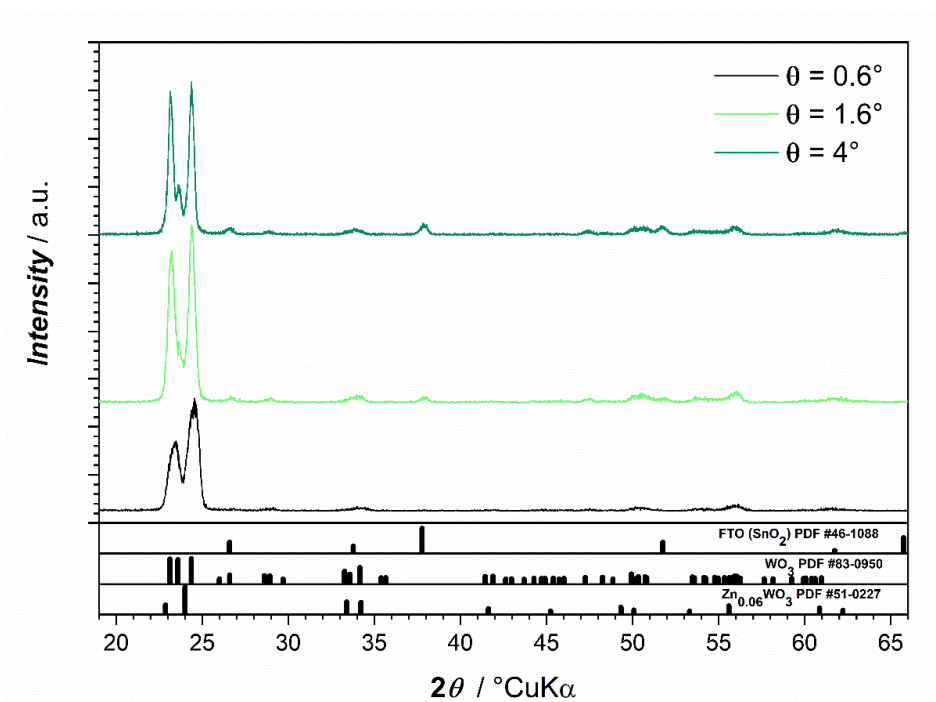


Figure 46. XRD of WO_3 modificiranog Zn

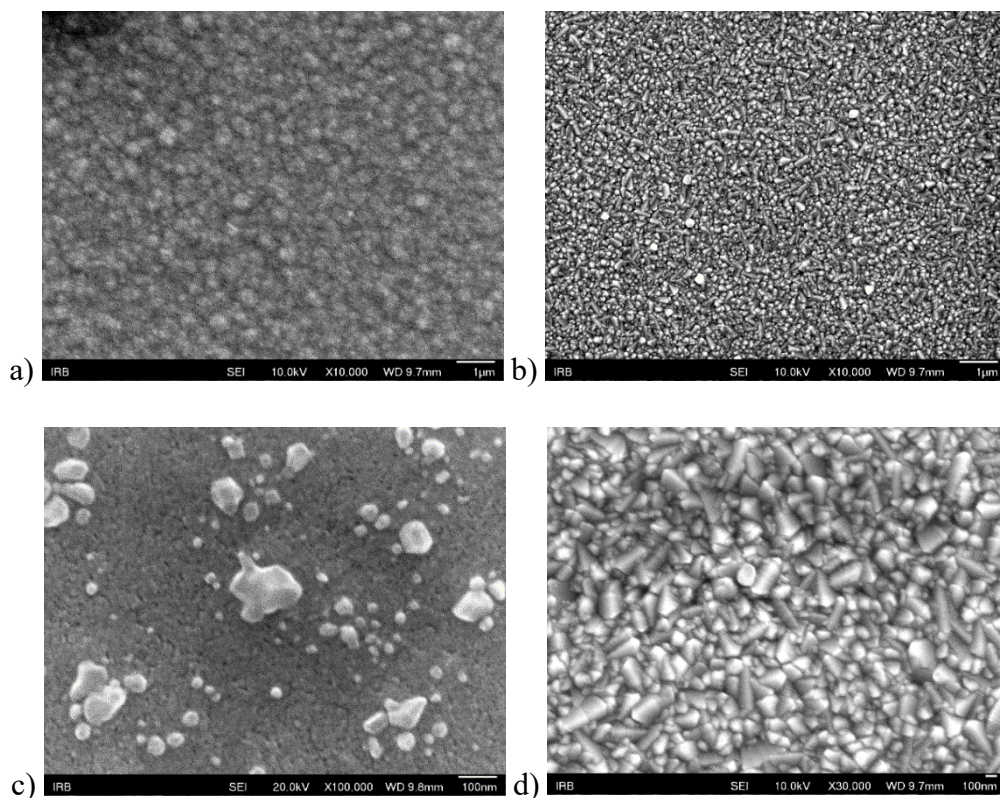
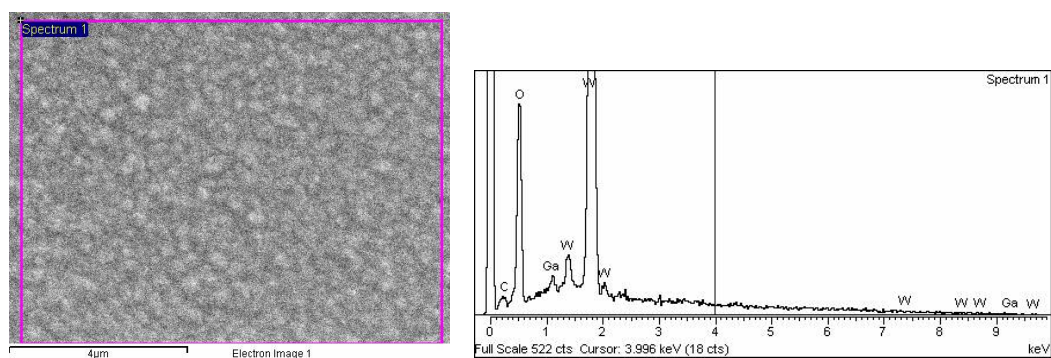


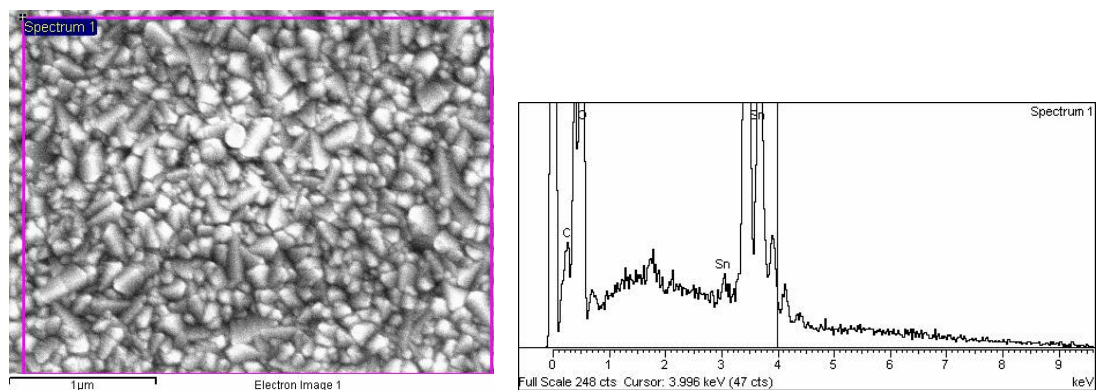
Figure 47. Images recorded by scanning electron microscopy method for a), c) Ga-modified WO₃ on FTO glass and b), d) FTO glass at two different magnifications

a)



Element	maseni%	atomski%	
C K	0.62	3.19	
O K	17.93	68.84	
Ga L	1.36	1.20	
W M	80.09	26.76	
Totals	100.00		

b)



Element	maseni%	atomski%	
C K	0.31	1.10	
O K	27.82	73.36	
Sn L	71.87	25.55	
Totals	100.00		

Figure 48. EDX analysis of samples for a) WO₃ modified with Ga on FTO glass and b) FTO glass

Table 1: Crystallite sizes, calculated from XRD patterns using the Scherrer equation and BET specific surface areas.

Sample name	Calculated anatase crystallite size (nm)	BET specific surface area (m ² /g)	Band-gap (eV)
TiO ₂	11	103	3.3
Pt-TiO ₂	14	81	3.3
Pt-TiO ₂ used	15	75	3.3
Pt-TiO ₂ used-calcined	15	/	/

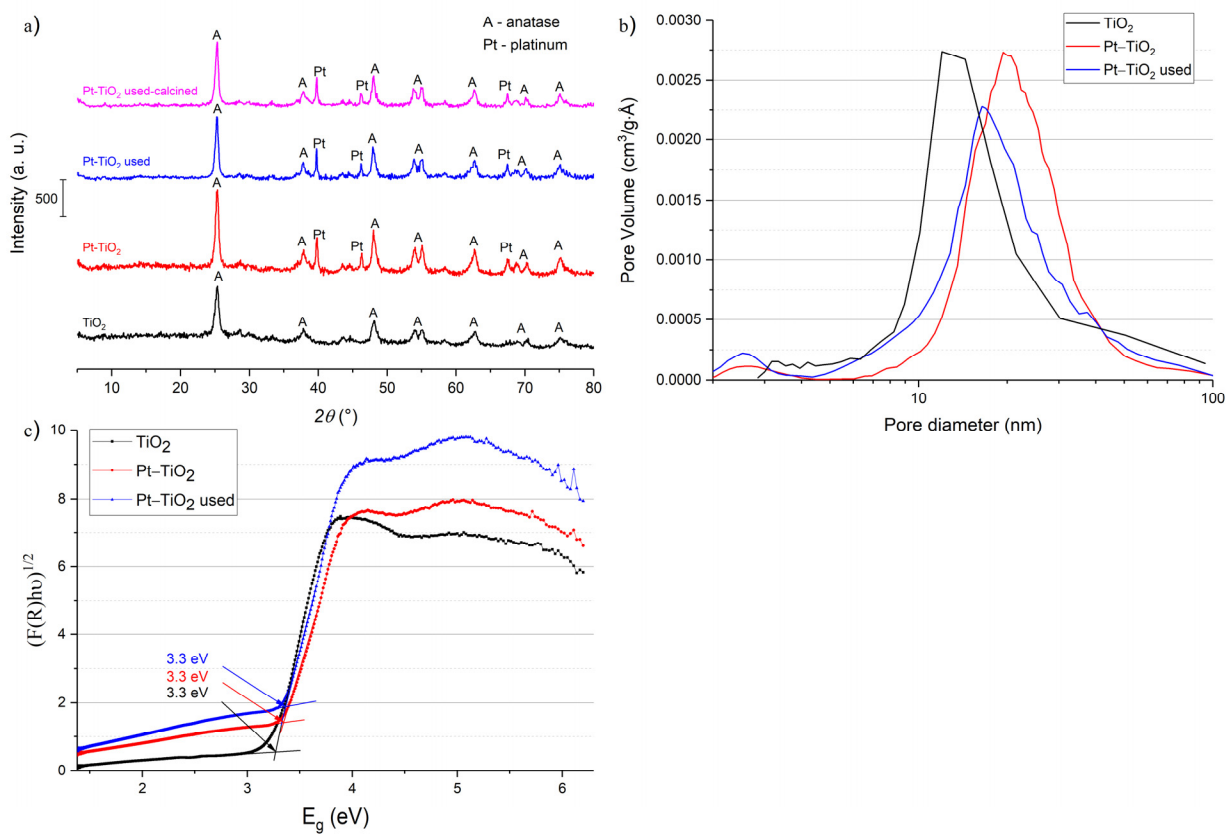


Figure 49. a) X-ray diffraction (XRD) patterns of the powder samples and b) Pore size distribution of the unmodified TiO₂, as well as samples before and after use in photocatalytic degradation, and c) Tauc plots used for determination of band gap values.

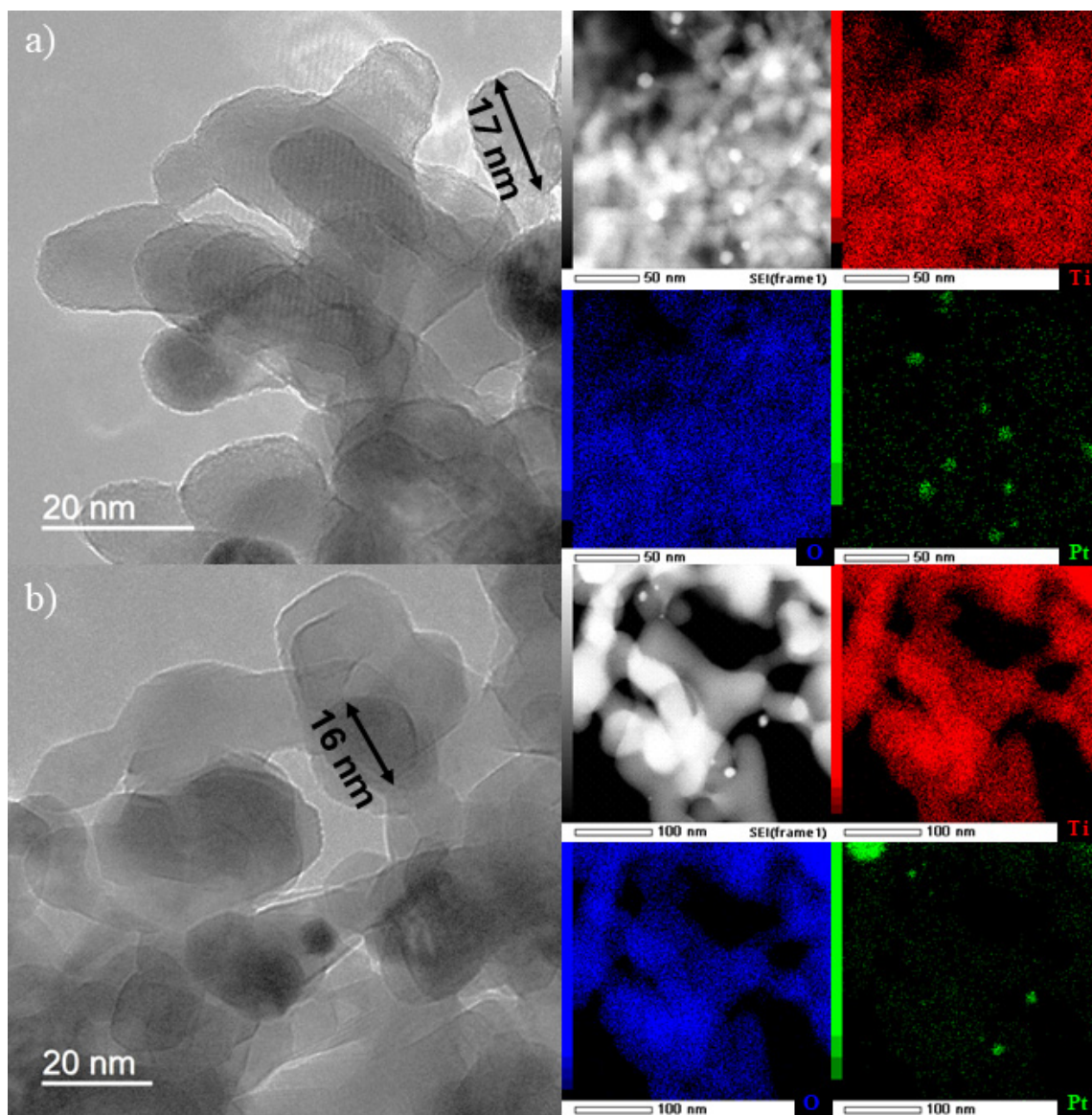


Figure 50. TEM images of Pt-TiO₂, a) before and b) after photocatalytic treatment and the corresponding elemental mappings.

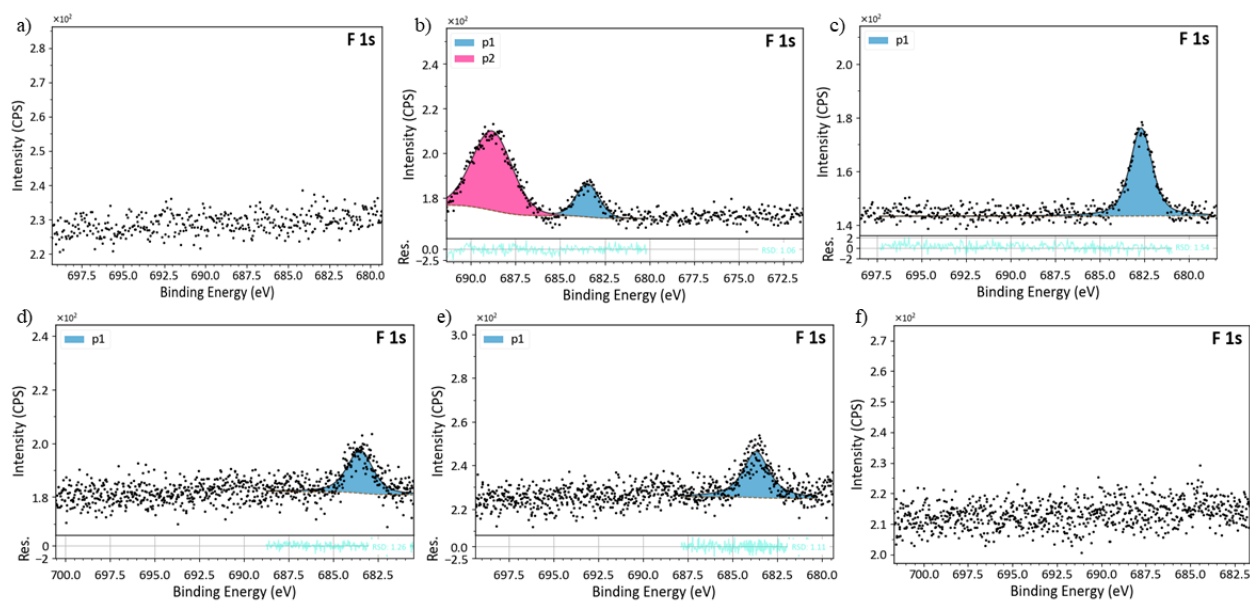


Figure 51. High-resolution F1s spectra of a) Pt–TiO₂, b) Pt–TiO₂ used, c) Pt–TiO₂ NaF, d) Pt–TiO₂ used–H₂O, e) Pt–TiO₂ used–NaCl and f) Pt–TiO₂ used–calcined.

Table 2: Quantitative XPS analysis of fluorine in samples.

Sample name	F (at %)
Pt–TiO ₂	/
Pt–TiO ₂ used	4.70
Pt–TiO ₂ NaF	2.20
Pt–TiO ₂ used–H ₂ O	0.90
Pt–TiO ₂ used–NaCl	0.60
Pt–TiO ₂ used–calcined	/

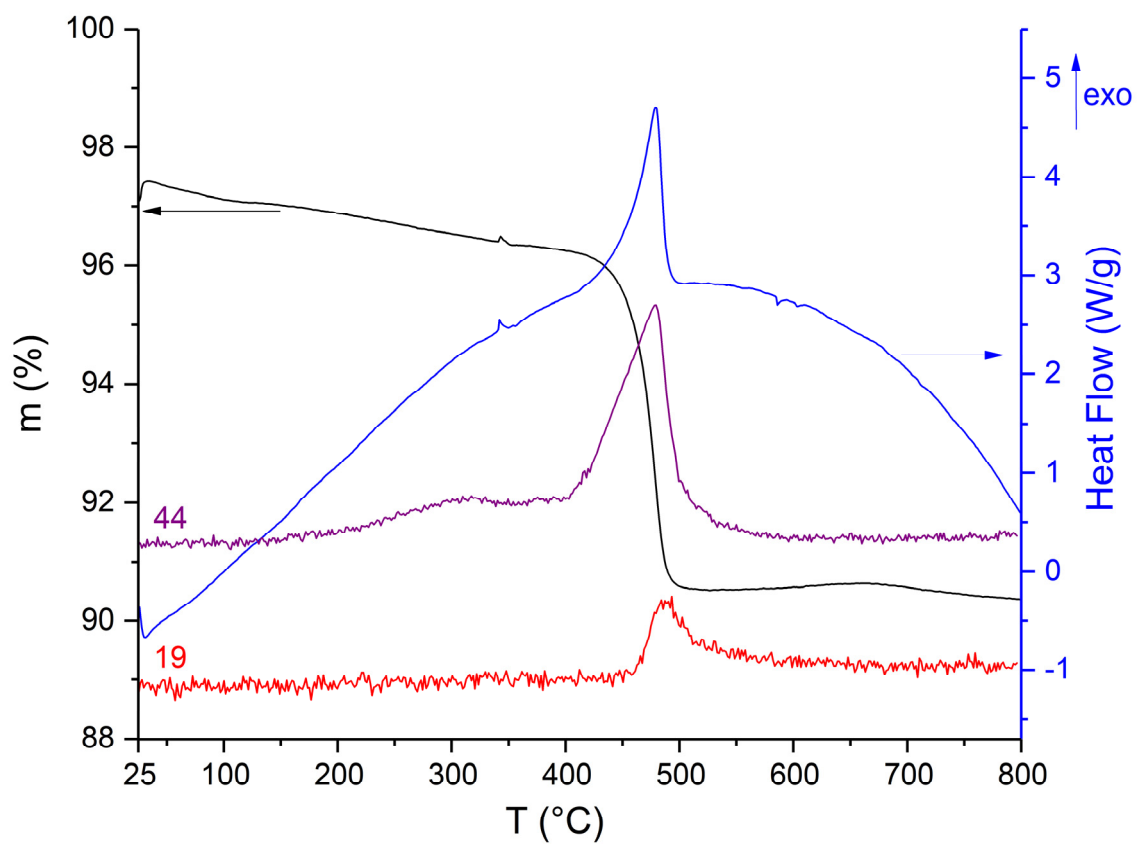


Figure 52. TG–DSC–MS analysis of the used photocatalyst.

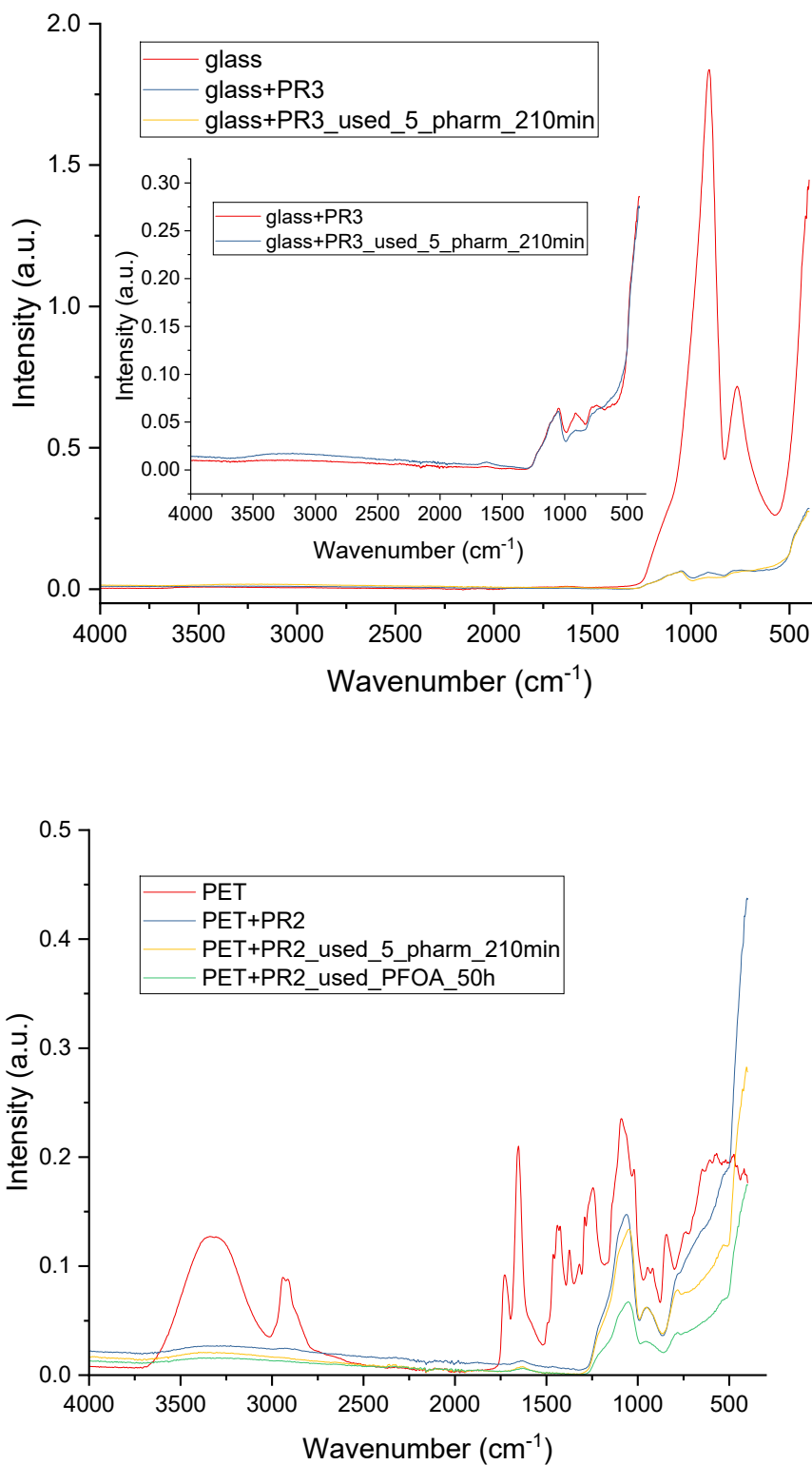


Figure 53: FT-IR spectra of S3N2 films on glass (up) and PET plastic (down)

