Supporting Information

Nanostructured Fe_2O_3/SnO_x Heterojunction Photocatalyst Fabricated by Co-Precipitation and Spin Coating for Efficient Photoelectrochemical Wastewater Treatment

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1: Variation of pH as a function of NH_4OH

The initial pH of the precursor solution was about 1, indicating a highly acidic medium. Ammonium hydroxide (NH_4OH) was added dropwise under continuous magnetic stirring (1500 rpm) at room temperature to gradually increase the pH. Slow addition of NH_4OH helped to avoid local supersaturation and allowed controlled precipitation. The pH was monitored using pH indicator paper, and NH_4OH was added until the pH reached ~ 10. At this stage, iron hydroxide precipitated. **Figure S1** shows the variation of pH as a function of the volume of NH_4OH introduced during the co-precipitation production of Fe_2O_3 nanoparticles.

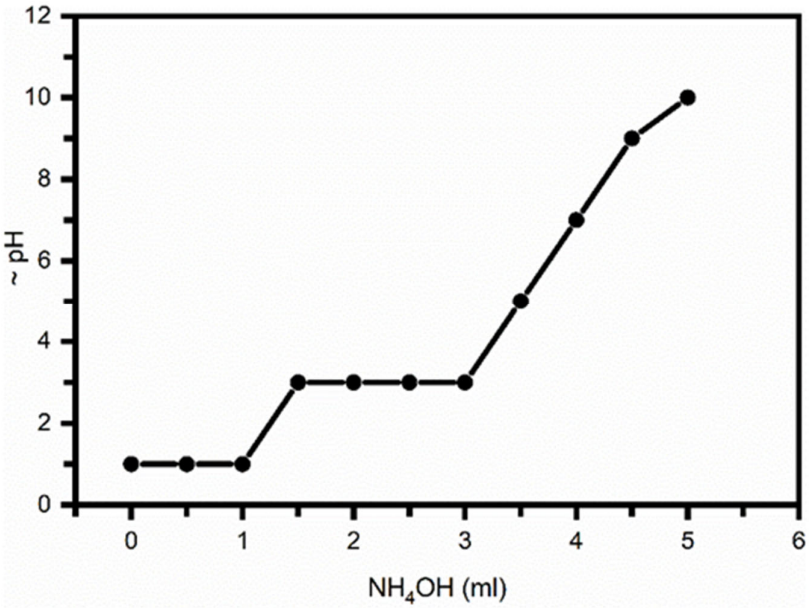

Figure S1: pH variation in the solution in relation to the volume of NH_4OH introduced during the co-precipitation production of Fe_2O_3 nanoparticles. Using pH indicator paper, the pH was monitored as NH_4OH was gradually added, continuously stirred (at 1500 rpm), until the solution reached pH ~ 10, at which point iron hydroxide precipitation occurred.

2: SEM analysis of Fe_2O_3 nanoparticles

A precursor concentration of 0.5 M was selected to ensure sufficient nucleation and reproducible synthesis of Fe_2O_3 nanoparticles via co-precipitation. **Figure S2** shows the SEM micrograph of as-synthesized Fe_2O_3 nanoparticles at 0.5 M concentration of $FeCl_2{\cdot}6H_2O$ and the corresponding particle size distribution histogram. The chosen concentration provided adequate supersaturation for nucleation and a good yield of Fe_2O_3 nanoparticles for subsequent incorporation into SnO_x thin films.

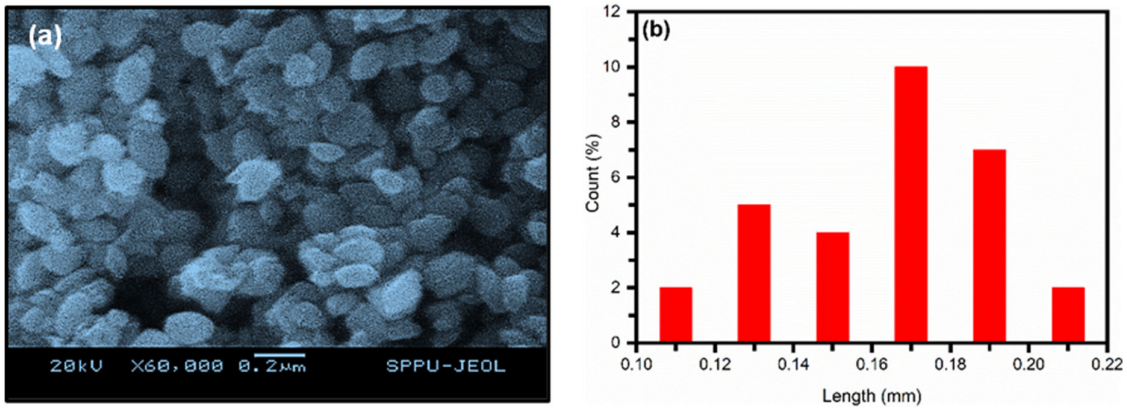

Figure S2: (a) Synthesized SEM micrograph of Fe_2O_3 nanoparticles, **(b)** Particle size distribution histogram.

3: Williamson-Hall (W-H) plots

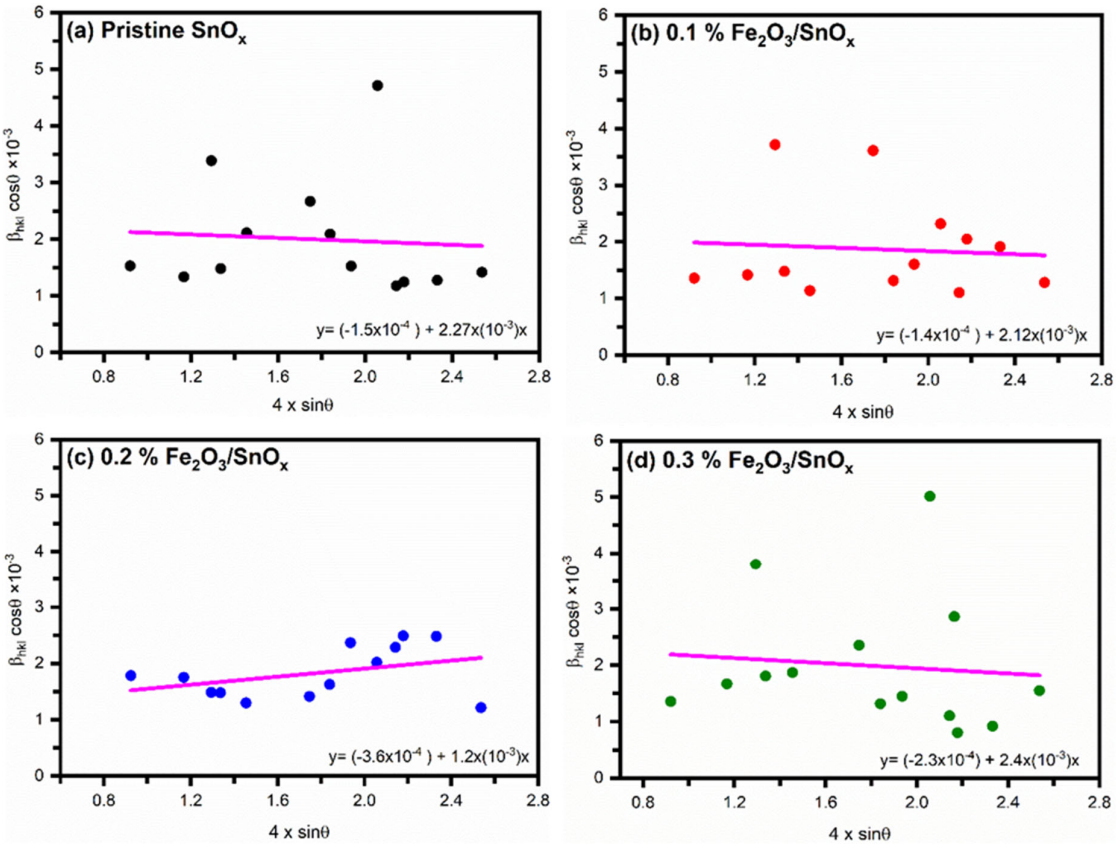

Figure S3: Williamson-Hall (W-H) plots **(a)** Pristine-SnO_x, **(b)** 0.1 % Fe_2O_3/SnO_x, **(c)** 0.2 % Fe_2O_3/SnO_x, and **(d)** 0.3 % Fe_2O_3/SnO_x heterojunction thin films.

4: Calculations of the relative concentration of oxygen vacancies

The calculated values of the relative concentration of oxygen vacancies in pristine SnO_x and 0.1-0.3 % Fe_2O_3/SnO_x samples.

Table T1: The relative oxygen vacancy concentration was estimated from the ratio of defect oxygen to the total lattice and defect oxygen peak areas.

Sample	Lattice O area	Defect O area	Oxygen Vacancy (%)
SnO_x	29422	9710	24.81
0.1 % Fe_2O_3/SnO_x	10200	4373	30.01
0.2 % Fe_2O_3/SnO_x	10129	6129	37.70
0.3 % Fe_2O_3/SnO_x	7590	2400	24.02

5: Thickness Measurements

The thickness of the photoelectrode films was measured using cross-sectional SEM analysis, as shown in **Figure S4**. The pristine SnO_x film is ~ 1.4 µm thick. The Fe_2O_3-mixed SnO_x films showed thicknesses of ~ 1.6 µm, 1.7 µm, and 1.3 µm, respectively.

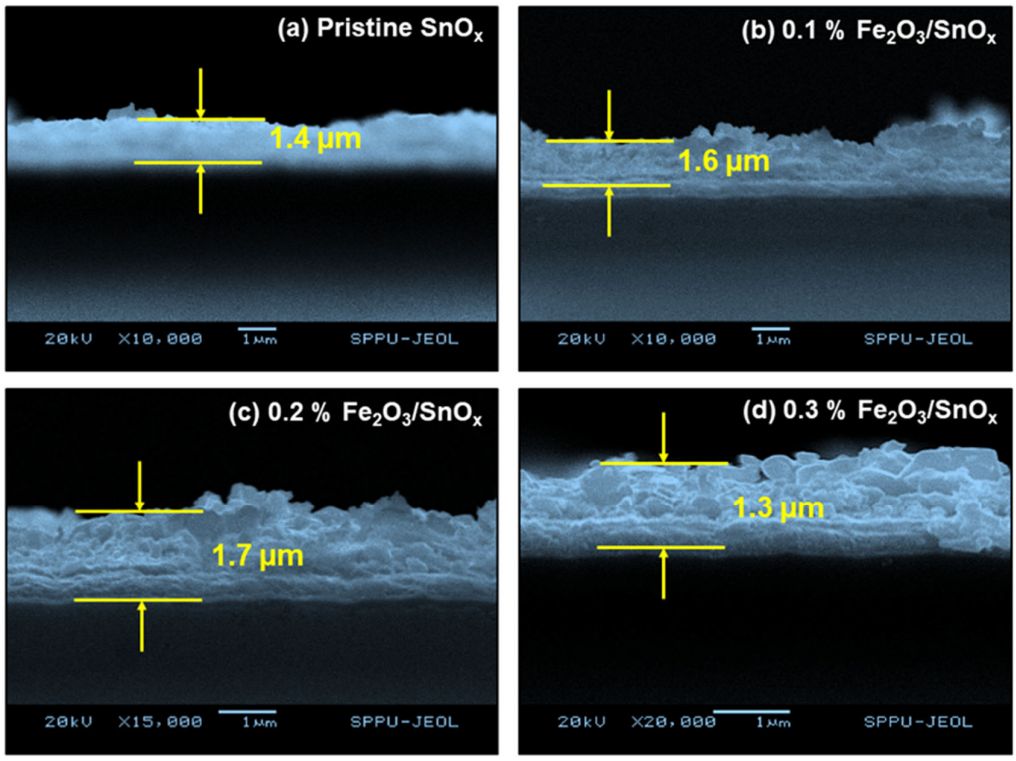

Figure S4: Cross-sectional SEM micrographs of **(a)** Pristine-SnO_x, **(b)** 0.1 % Fe_2O_3/SnO_x, **(c)** 0.2 % Fe_2O_3/SnO_x, and **(d)** 0.3 % Fe_2O_3/SnO_x for thickness measurement.

6: Scanning Electron Microscopy Elemental Mapping

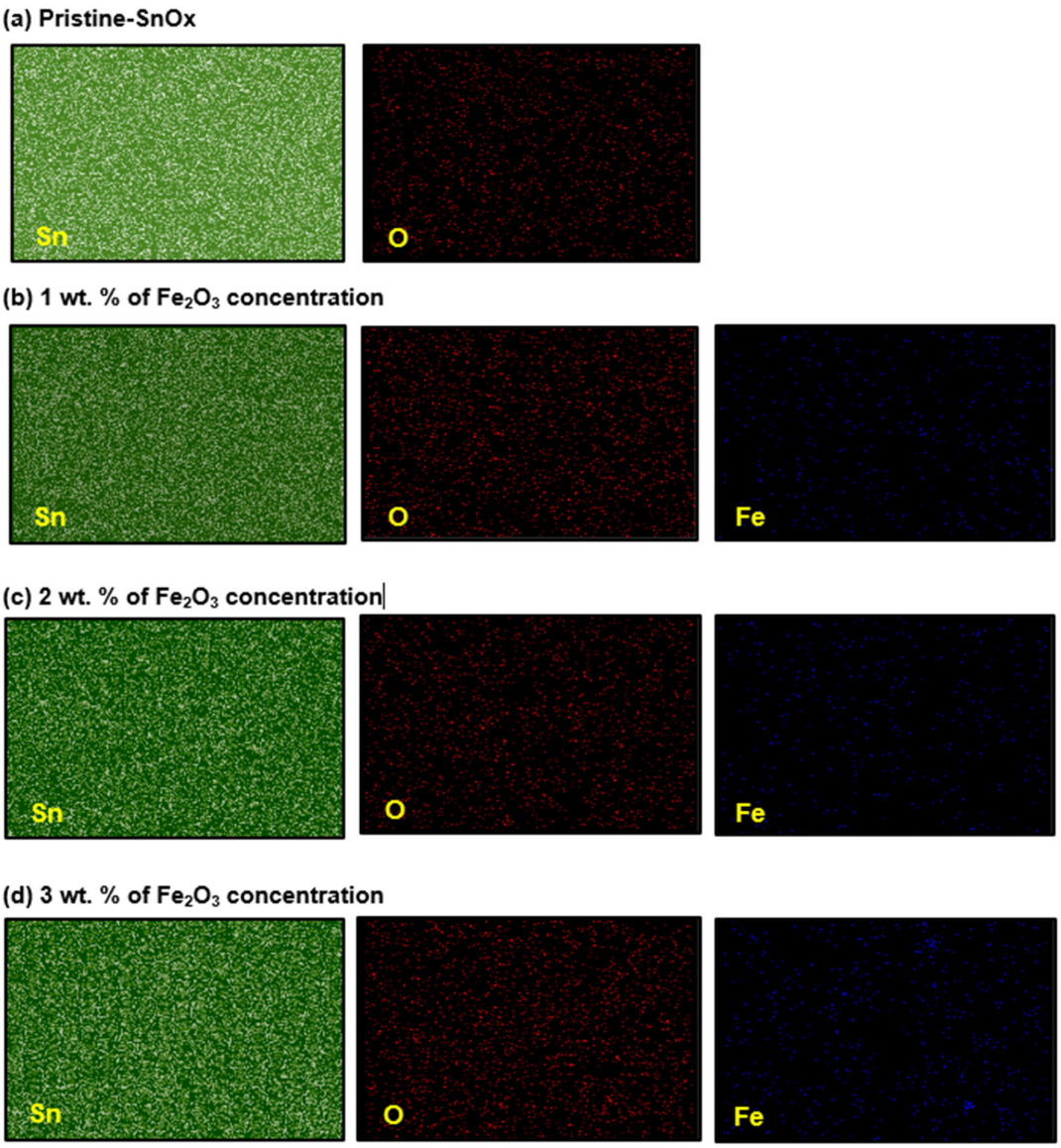

Figure S5: Elemental mapping of the Pristine-SnOx and Fe_2O_3/SnOx heterojunction thin films with different wt. % of Fe_2O_3 concentrations

7: Angle of Contact Measurements

Figures S6(a)-S6(d) show the contact angle measurement image for Pristine-SnOx and Fe_2O_3/SnOx heterojunction thin films with different wt. % of Fe_2O_3 concentrations.

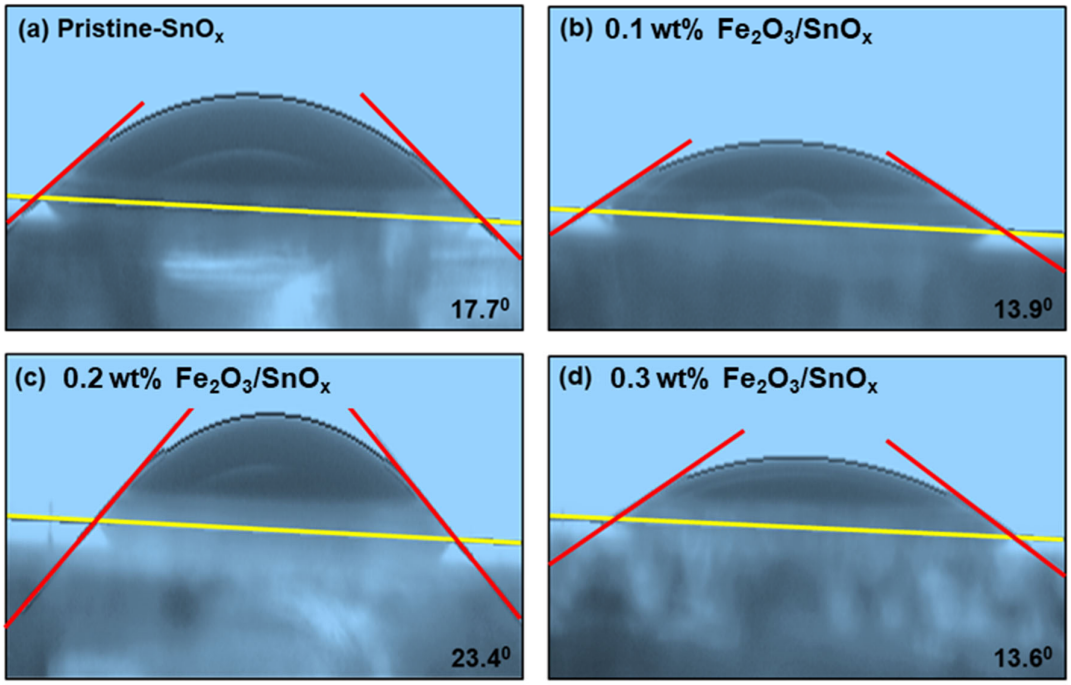

Figure S6: Contact angle measurement of **(a)** SnO_x, **(b)** 0.1 wt % Fe_2O_3/SnO_x, **(c)** 0.2 wt % Fe_2O_3/SnO_x, and **(d)** 0.3 % Fe_2O_3/SnO_x heterojunctions.

8: Chronoamperometric Photocurrent Stability Test

The Chronoamperometric photocurrent stability of the optimized 0.2 % Fe_2O_3/SnOx photoelectrode measured for 8000 s under continuous illumination is shown in **Figure S7**.

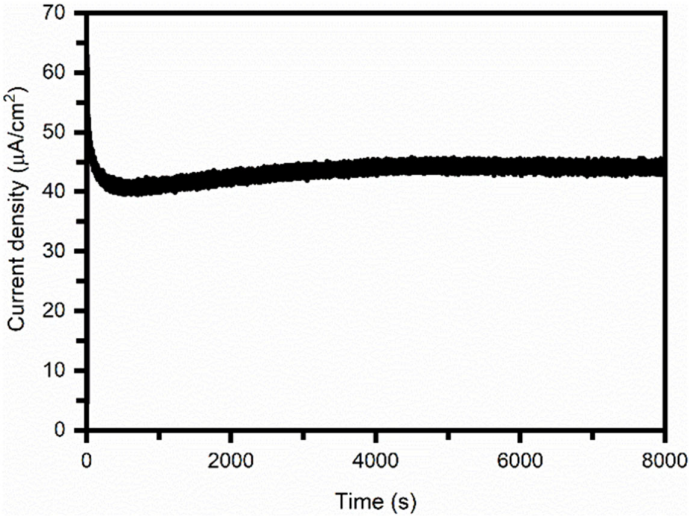

Figure S7: Chronoamperometric photocurrent stability of the 0.2% Fe_2O_3/SnOx photoelectrode measured for 8000 s under continuous illumination in 1 M Na_2SO_4 electrolyte at an applied bias of 0.5 V (vs. SCE). The light intensity was 100 mW/cm^2, calibrated using a conventional silicon photodetector, with a Pt electrode used as the counter electrode.

9: SEM and EDS Analysis after 8000 s

The surface morphology and compositional analysis of the optimized 0.2 % Fe_2O_3/SnO_x photoelectrode, measured after 8000 s of continuous illumination, are shown in **Figure S8**.

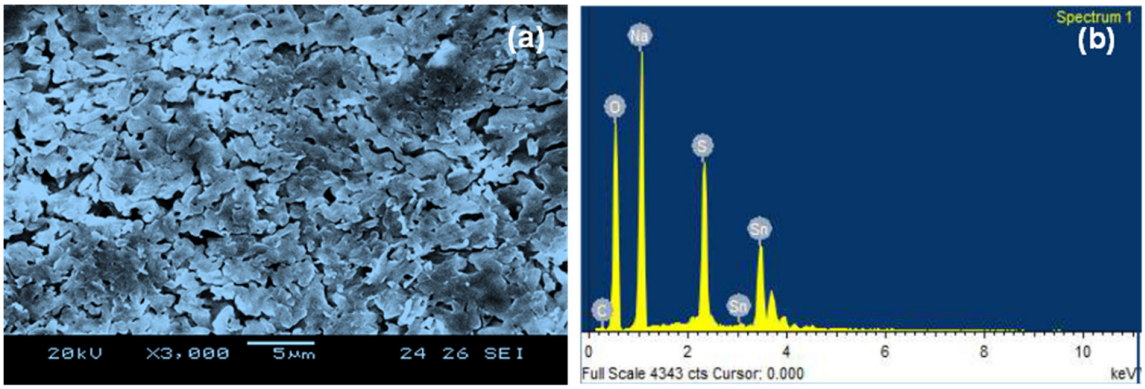

Figure S8: (a) After an 8000-second stability test, a SEM image of the 0.2 % Fe_2O_3/SnO_x thin film revealed a compact and granular morphology. **(b)** The EDS spectrum shows good compositional stability after extended operation and confirms the presence of Sn, O, and Fe elements, together with Na and S signals coming from the Na_2SO_4 electrolyte.