ZnO-ZnS Heterojunctions: A Potential Candidate for Optoelectronics Applications and Mineralization of Endocrine Disruptors in Direct Sunlight

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Supporting Information

S1 - Characterization and Instrumental Methods

Powder X-ray diffraction (XRD) data of ZSx materials was collected on a Rigaku X-ray diffractometer (DMAX IIIVC) equipped with a Ni-filtered Cu Kα radiation (λ = 1.542 Å) and graphite crystal monochromator. Selected materials XRD data were collected on Philips X’Pert Pro diffractometer. The data was collected with a step size of 0.020° and a scan rate of 0.5°/min. The observed inter planar d spacing was corrected with respect to Si. The BET-surface area and BJH-pore size distribution of the materials were analyzed on a Quadrasorb SI instrument at 77 K; the measurement was conducted after the materials had been degassed at 573 K. Scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) measurements were performed on an SEM system (Leica, Model Stereoscan-440) equipped with EDX analyzer (Bruker, D451-10C Quantax 200 with X-flash detector) attachment. X-flash 4010 detector was employed for fast and high resolution real time spectrometry and elemental mapping. EDX spectra were recorded in the spot-profile mode by focusing the electron beam onto specific regions of the sample. However materials composition reported in this communication (Table 1) is based on the data collected over large areas, and it is also in agreement with chemical analysis of metal ions. HRTEM of the materials was conducted on a FEI TECNAI 3010 electron microscope operating at 300 kV (Cs = 0.6 mm; 1.6 Å resolution). Thermal analysis experiments were measured in Perkin-Elmer’s Diamond TG/DTA at a rate of 10 °C/min in air and/or nitrogen atmosphere.

Diffuse reflectance UV–Vis measurements were carried out on a Shimadzu spectrophotometer (model UV-2550) with spectral-grade BaSO4 as reference material. Raman spectra were recorded on a Horiba JY LabRAM HR 800 Raman spectrometer coupled with microscope in reflectance mode with 633 nm excitation laser source, and a spectral resolution of 0.3 cm⁻¹. X-ray photoelectron spectra (XPS) were recorded on VG Microtech Multilab ESCA 3000 spectrometer equipped with non-monochromatized Al Kα (1486.6 eV) or Mg Kα(1253.6 eV) x-ray sources. Selected spectra, especially N 1s core level, were recorded with both the above sources to eliminate the overlap between Zn-LVV Auger levels. Secondary ion mass spectrometry (SIMS) studies were carried out with a QMS-based instrument (Hiden Analytical). Bombardment was done with 5 keV O and Cs ions. Primary ion current was 400 nA (oxygen beam) and 100 nA (cesium beam). Beam was rastered over an area of 1000 µm²; however the secondary ions were collected from the central 200 µm² area.

Photocatalytic Activity and Photocurrent Measurements. Photocatalytic degradation of ECD, such as 2,4 dichlorophenol (2,4-DCP) and endosulphan, was conducted in a borosil RB flask for different periods of time under direct sun light irradiation on the terrace of the NCL, Pune (GPS coordinates: 18°32’30.786” N and 73°48’41.2884” E). 25 ppm ECD solutions were prepared initially and used for photocatalytic mineralization experiments. In a typical experiment, 50 mg of the catalyst was dispersed in 100 ml solution containing any ECD (2,4-DCP or endosulphan) and irradiated under direct sun light. Few irradiation experiments were conducted with a 400 W mercury lamp (λ = 200-400 nm) using a flow-type double-jacketed quartz reactor. Before any irradiation, the reaction mixture was stirred for 30 min in the dark and irradiation was conducted for different time period. After irradiation, 3 ml of solution was
periodically withdrawn to measure UV-visible spectrum, and then the same solution was added quickly to the original solution and irradiation was resumed. GC-MS analysis was performed for endosulphan degradation intermediates or products (GC model: Agilent-7890B with DB-5MS column; 30 m x 0.250 mm x 0.25 micron; MS model: Agilent-5977A MSD). NIST library was referred to analyze various endosulphan fragments and fragment patterns. Photoreponse of the material was carried out by chronoamperometry measurements which was recorded at 0 V using a Gamry potentiostat (model 3000 potentiostat) in a conventional three-electrode test cell with Ag/AgCl as the reference electrode and a platinum foil as the counter electrodes with an Oriel Instruments 300 W xenon arc lamp equipped with an AM1.5 filter. It is to be mentioned that the immediate response for shutter oscillation highlights the photofunctional behavior of the material. As long as the material is irradiated, the current remains constant; it demonstrates production of the current is exclusively due to the photoresponse.
Thermal stability of ZSx was explored with XRD after ex-situ calcination of ZS4 and ZS1 at different temperatures for 4 hours in air and the results are shown in Figure S1a and b, respectively. No significant change in the intensity of ZnS and ZnO features were observed below 400 °C. However, intensity of ZnS peaks decreases and a simultaneous increase in the intensity of ZnO features occurs, especially for the materials calcined ex-situ ≥500°C. Above changes are attributed to the systematic oxidation of ZnS to ZnO under air atmosphere with an increase in calcination temperature. Although the XRD patterns of ZS4 recorded after calcination at 300 and 500 °C is comparable for ZnS features, a significant increase in ZnO features hints an increase in ZnO crystallite size due to slow oxidation of ZnS. However ZS4 calcined at 600 °C shows very low intensity for ZnS indicating an enormous size reduction of ZnS crystallites. Above results are compared with XRD pattern of physical mixture of ZnO (30 %) and ZnS (70 %). A glance at the results indicates a difference in the intensity patterns of prominent diffraction peaks in Figure S1a. (100) facet shows the highest intensity than other facets of ZnS on ZS4; however (002) facet shows higher intensity in the physical mixture and pure ZnS. Results from other characterization also provide strong and direct support towards ZSx composites with heterojunctions and this will be discussed later. No sulfate formation has been observed for ZS3 and ZS4 materials calcined up to 600 °C; however the oxidation of ZnS to ZnO is expected to occur through sulfate formation, as explained in thermal analysis later (vide infra Fig. 4 in the main manuscript). ZS4 (and ZS3) calcined at 800 °C shows features only due to ZnO suggesting the total conversion of ZS4 (or ZS3) to ZnO. Except for peak narrowing, ZS1 material calcined at 550 °C (Figure S1b) does not show any significant changes in XRD. Upon further calcination to 800 °C it shows exclusive ZnO features. Similar trend was observed for ZS2 material, indicating the decomposition of sulfate features to ZnO.
Figure S2. Elemental mapping of ZSx materials for (a-c) ZS2 and (d-e) ZS4. Color coding for different elements are shown on the images (N – red, S – green and Zn – blue, O-cyan). Uniform distribution of all the elements can be seen over the large area of >1 mm$^2$. Elemental mapping of all the elements have been carried out and shown with color coding for different elements. High and low intense (or diffused) color indicating the particular element’s high and low content, respectively, in a particular area/spot. Fig.S2c and S2f shows only N and S mapping of the above materials to show the homogeneous distribution of all atoms.

EDX results confirm the homogeneous distribution of doped elements at microscopic level over a large area and indicating the effectiveness of the preparation method. A careful look at the elemental map (Figure S2b and e) reveals the association of Zn and S more on ZS4 than ZS2, suggesting the large percentage of ZnS in ZS4 and suggesting the composite nature. It is also to be noted that the atom percent measured through EDX on individual particle differs significantly, and values reported in Table 1 (in main manuscript) are the average values obtained over large areas, as shown in Figure S2. A glance at ZS2 (Figure S2b) and ZS4 (Figure S2e) highlights the change in color from dark blue to light blue due to the change in surface composition from a predominant ZnO to ZnS composition, respectively. An increase in sulfur content is evident from an increase in green color density from Figure S2c to S2f. Indeed the red color (for N) could be seen easily in Figure S2c than Figure S2f, indicating a decrease in N-content. Systematic color variation was observed with increasing S-content from ZS1 to ZS4.
Figure S3. (a) Zn 2p<sub>3/2</sub> core level appears between 1021.5 to 1022.1 eV indicating the oxidation state of Zn to be 2+. (b) O 1s core level BE for ZSx materials appears at 531.8 eV which is significantly different from Z1 and ZnO (530.5 eV). O 1s peak that appears at 530.5 eV is attributed to typical oxide peak of ZnO. However, in ZSx the O 1s peak at 531.8-532.0 eV was observed indicating the formation of sulfate. Indeed S 2p core level too shows sulfate features even with ZS4. Nonetheless sulfate formation is mostly restricted to surface and no features corresponding to sulfate has been observed in any bulk characterizations, such as XRD, Raman, SIMS. Observation of sulfide feature in S 2p with no oxide feature from ZnO suggests that sulfate feature is likely to be found on ZnO clusters. (c) Survey spectra recorded for ZSx is given for comparison.
Figure S4. IPCE measurements made with PV cells (reported in Fig. 11 in the manuscript).
Figure S5. Photocatalytic degradation of 2,4-DCP under direct sun light with ZS3 in the presence of H₂O₂. Magnified image is shown in the inset.
Figure S6. First-order kinetics plots of photocatalytic degradation activity for 2,4-DCP with ZSx under (a and b) direct sun light, and (c) UV-light and sunlight with H$_2$O$_2$. Rate constant calculated are also given.
Figure S7. (a) GC, and (b, c) MS results of virgin endosulfan before reaction/photocatalytic decomposition.
Figure S8. GC and the MS (1-10) results of endosulfan fragments after 60 h reaction under direct sunlight with ZS4 catalyst.
Table S1: Identification of various mass fragments and their selectivity

| No. | Retention Time (R_t min.) | Molecular weight | Chemical composition and most Probable molecule | Probability (%) | Selectivity (%) |
|-----|--------------------------|------------------|-------------------------------------------------|----------------|-----------------|
| 1.  | 3.37                     | 148              | C_{10}H_{12}O                                   | 97.9           | 0.98            |
| 2.  | 4.12                     | 122              | C_8H_{10}O - α-methyl-phenyl alcohol            | 50.1           | 1.09            |
| 3.  | 4.22                     | 120              | C_8H_{10}O - Acetophenone                       | 69.8           | 46.1            |
| 4.  | 4.42                     | 136              | C_9H_{12}O - 2-phenyl-2-propanol                | 91.9           | 45.6            |
| 5.  | 5.65                     | 130              | C_8H_{18}O - 1-Octanol                          | -              | 0.57            |
| 6.  | 8.24                     | 112              | C_8H_{18}O - 1-Octene                           | -              | 0.43            |
| 7.  | 9.66                     | 207              | C_9H_{20}Cl_3 - 1,4,7-trichloro-2-methyl bicyclo[2.2.1]hepta-2,5-diene | - | 0.16 |
| 8.  | 10.68                    | 222              | C_{12}H_{14}O_4 - Diethyl Phthalate             | 81.0           | 1.72            |
| 9.  | 17.15                    | 342.8            | C_8H_{16}Cl_6O - ES-ether                       | -              | 0.42            |
| 10. | 17.4                     | 360              | C_8H_{16}Cl_6O_2 - ES-diol                      | 84.7           | 2.8             |