Electronic Supplementary Material (ESI) for Environmental Science: Nano.

Supplementary Information

Ionic Liquid Assisted Synthesis of Novel PANI/$ZnWO_4$/WO_3 Ternary Nanocomposite: A Facile Double Electron Transfer Photocatalyst for Efficient Degradation of Herbicide

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Reagents and materials

All reagents were used of analytical grade without further purification. Sodium tungstate (Na_2WO_4), Glyphosate and Zinc nitrate hexahydrate ($Zn(NO_3)_2.6H_2O$) were purchased from Sigma Aldrich. Other chemicals used in this report were obtained from Hi-Media which include ammonium persulfate ($((NH_4)_2S_2O_8)$), aniline, H_2O_2 (30%), ethanol, H_2SO_4 (98%), HCl, NaOH. Agar-agar type I (Himedia), 1X Phosphate buffer saline (PBS, Himedia), 1.5ml eppendorf tubes (Tarsons), 1ml micro-pipette (accuppet), USB Stereo zoom microscope (500X).

Sample Synthesis

Synthesis of 1- butyl 3- methyl imidazolium chloride (BMIMCl) IL

First of all, 1mol of chloro-butane and 1mol of methyl imidazole which were taken in a 250 ml RB attached with a reflux condenser. The mixture was kept under constant stirring for 72 h at 70˚C. Then, the reaction mixture was cooled at 4 ˚C for 24 h. Afterwards, the mixture was washed repeatedly with ethyl acetate to remove unreacted substrates. Then the remaining sample was dried via rotary evaporation which is followed by vacuum drying at 70˚C for 24 h. The final yellowish thick liquid is 1- butyl 3- methyl imidazolium chloride (BMIMCl) IL.

Synthesis of $ZnWO_4$

$ZnWO_4$ was prepared by BMIMCl IL-assisted solvothermal method. In a typical procedure, 0.005 mole of $Zn(NO_3)_2$, $6H_2O$ and same amount of Na_2WO_4 was added to a 50 ml of DI water and BMIMCl IL mixture solution. The whole reaction mixture was kept under mechanical stirring for 30 min. The pH of the solution was balanced at 3 before transferring the whole solution to the Teflon-lined stainless steel autoclave. The reaction was kept at 180ºC temperature for 18 h. Thereafter, the reaction was cooled to room temperature naturally. The white precipitates were washed with ethanol and DI water followed by drying at 70ºC for 8 h before further characterization.

Synthesis of WO_3

Similarly, WO_3 was also prepared by BMIMCl IL-assisted solvothermal method. 0.005 mole of Na_2WO_4 was added to 50 ml of DI water and BMIMCl IL mixture solution. The resultant reaction mixture was kept under mechanical stirring for 30 min. The pH of the solution was adjusted to 3 with 0.1 M HCl solution. The resultant mixture was transferred to the same autoclave where it was kept at 180ºC temperature for 18 h. Thereafter, the reaction was cooled naturally. The final solid residuewas washed with ethanol and DI water followed by drying at 70ºC for 8 h before further characterization.

Synthesis of PANI-$ZnWO_4$ and PANI-WO_3

The PANI-$ZnWO_4$ and PANI-WO_3 were synthesized by adopting an *in situ* chemical oxidation polymerization process using $(NH_4)_2S_2O_8$ as a suitable oxidant. Firstly, a certain amount (0.2 g) of $ZnWO_4$ and WO_3 each were dispersed in 30 ml of 0.1M HCl solution separately followed by ultra-sonication for 30 min. On the other hand, 1 ml of anilinewas added to the aqueous solution of BMIMCl (1-butyl 3-mrthyl imidazolium chloride) to make PANI solution which was then added toprevious resultant reaction mixtures. To each nanostructure reaction mixture, aqueous solution of $(NH_4)_2S_2O_8$ was added drop wise in a molar ratio of 1:1 ($(NH_4)_2S_2O_8$: Aniline). The polymerization process kept for 12 h under magnetic stirring at room temperature. The resultant residue was centrifuged and obtained by washing with ethanol. Finally, after drying in vacuum for 4 h at 70 ºC the PANI-$ZnWO_4$ and PANI-WO_3 binary nanocomposites were furnished.

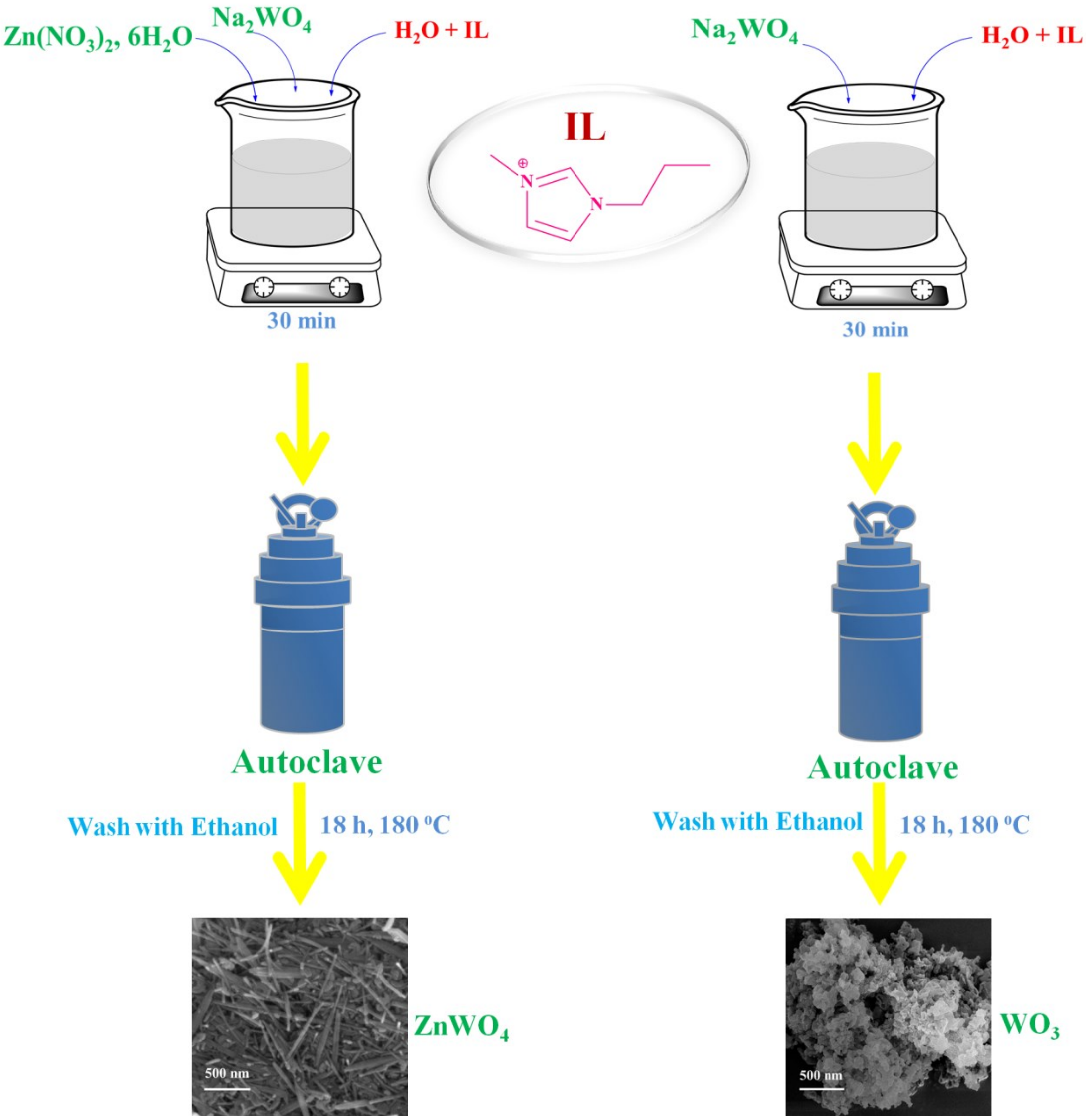

Fig. S1. Schematic illustration of IL-assisted solvothermal synthesis of $ZnWO_4$ and WO_3.

Instrumentation and measurements

The structural and morphological properties of the ternary heterojunction materials were analyzed by different available characterization tools. The nanocomposite detailed phases of the catalyst were analyzed by X-ray diffraction study using a Rigaku, Ultima-IV multipurpose system fitted with a Ni filtered CuKα (λ=1.5418 Å) X-ray source. The FTIR spectra of the product were recorded using a Perkin-Elmer FTIR spectrophotometer using KBr pellets. The UV–Vis-DRS spectra were recorded using a Jasco V-650 spectrometer with $BaSO_4$ integration sphere.

Solid-state Fluorescence (PL) spectra were obtained in the range of 350–600 nm (excitation wavelength 220 nm) using a Horiba Scientific Fluoromax-4 spectrometer. The morphology, size and structural properties of as synthesized nanomaterials were studied using FESEM (Nova NanoSEM microscope, 10 kV) and HRTEM (TECNAI 300 kV) techniques. The specific surface area of the hetero-junction materials was evaluated by BET method by N_2 sorption study using Quantachorme AUTOSORB 1 equipment. The XPS analysis was carried out on a K-Alpha instrument supplied by Thermo-scientific, UK, equipped with an Al Ka (1486.6 eV) monochromatic X-ray source. The measurement was carried out in the range of 0–1350 eV and at extremely high vacuum of 10–9 mbar. The dielectric parameters were measured using a computer-controlled impedance analyzer (HIOKI IMPEDANCE ANALYZER 1352) as a function of frequency (100 Hz to 1 MHz) at room temperature.

Photo-electrochemical measurements

Electrochemical impedance studies were performed with a HIOKI IMPEDANCE ANALYZER 1352 as a function of frequency between 100 Hz to 1 MHz at room temperature. It has a three electrode cell system where platinum (Pt) wire and Ag/AgCl were taken as the counter and reference electrodes respectively. Thin film samples were coated onto the ITO glass substrate which serves as the working electrode. The samples were prepared after 30 min sonication with 20 mL methanol to achieve homogeneous dispersion. Then, the prepared suspension was spin coated on to ITO substrates which are placed over a hot plate at 80 ºC. An aqueous solution of 0.5M Na_2SO_4 was used as an electrolyte. Again, the photocurrent responses with time and Mott-Schottky measurements were performed using electrochemical analyzer at kHz frequency where also aqueous 0.5M Na_2SO_4 was considered as the electrolyte.

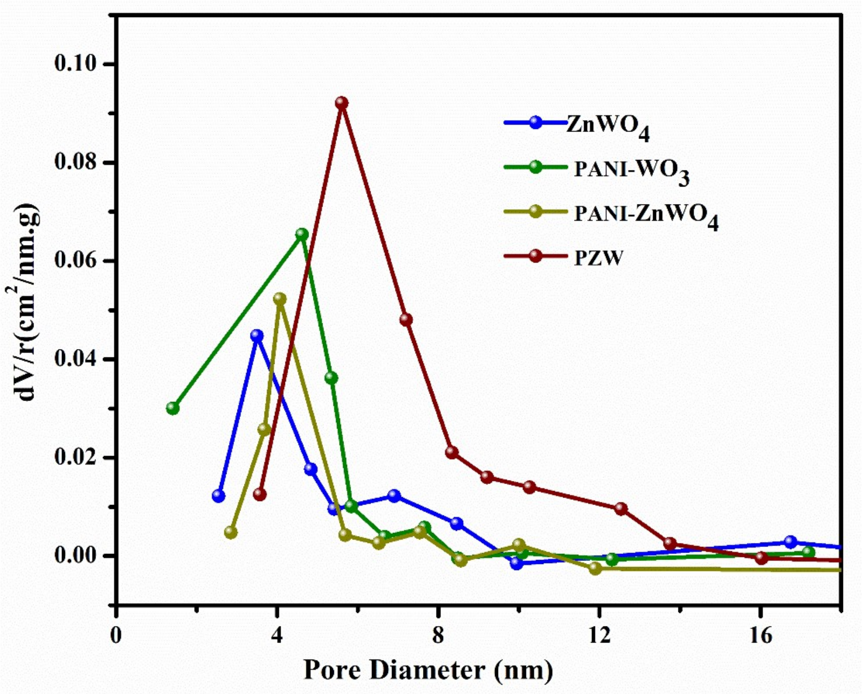

Fig. S2. Pore size distribution of $ZnWO_4$, PANI-$ZnWO_4$, PANI-WO_3 and PZW.

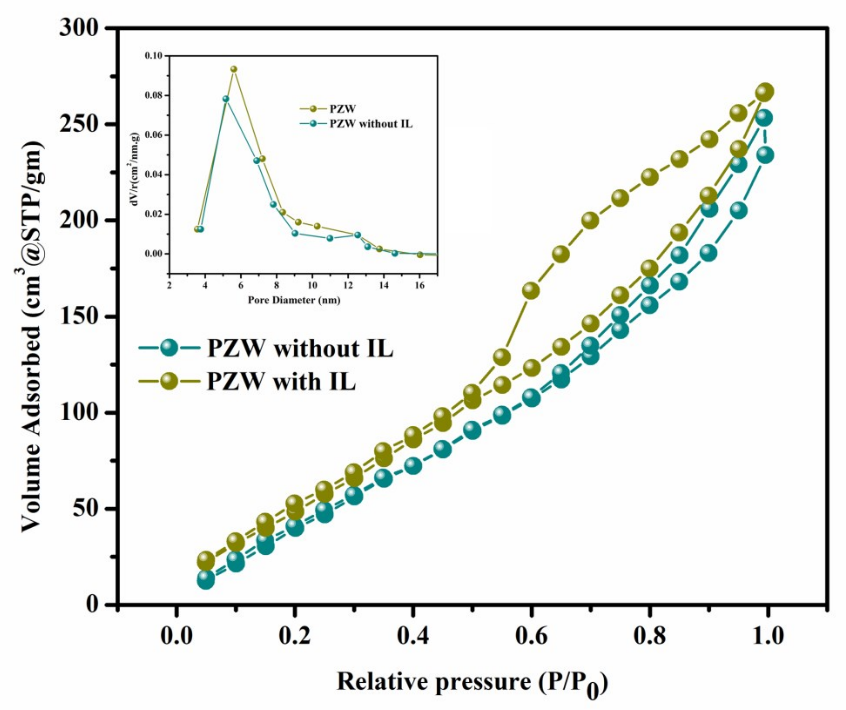

Fig. S3. N_2 adsorption-desorption analysis of PZW with IL and PZW without IL, Pore size distribution of PZW with IL and PZW without IL (inset).

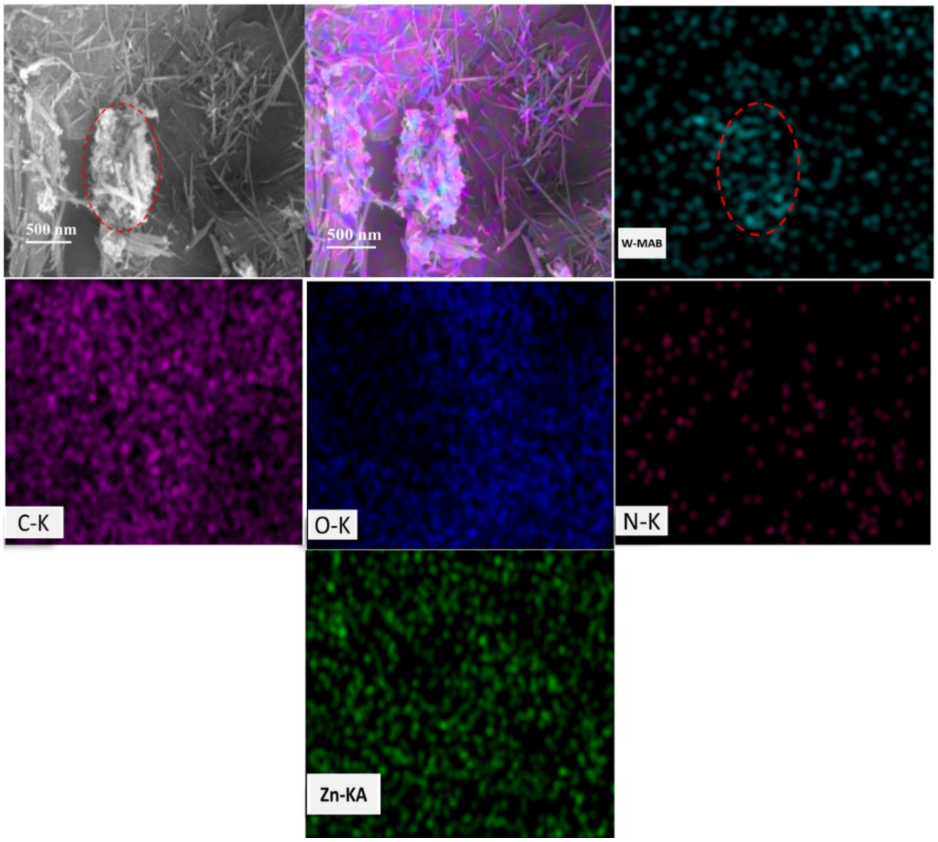

Fig. S4. Elemental mapping images of PZW nanocomposite materials.

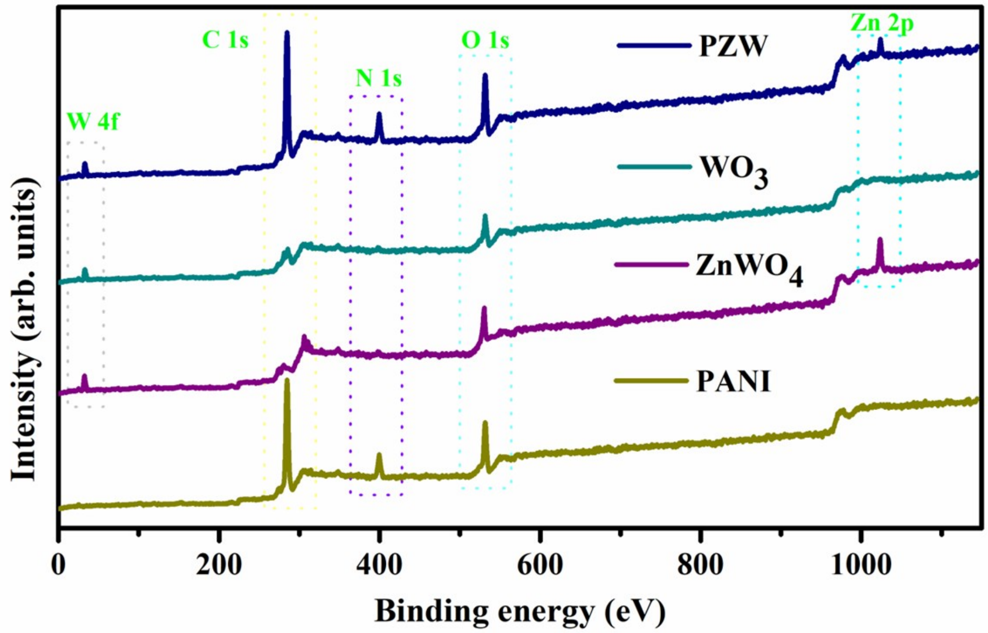

Fig. S5. Typical XPS survey spectra of PANI, $ZnWO_4$, WO_3, and PZW.

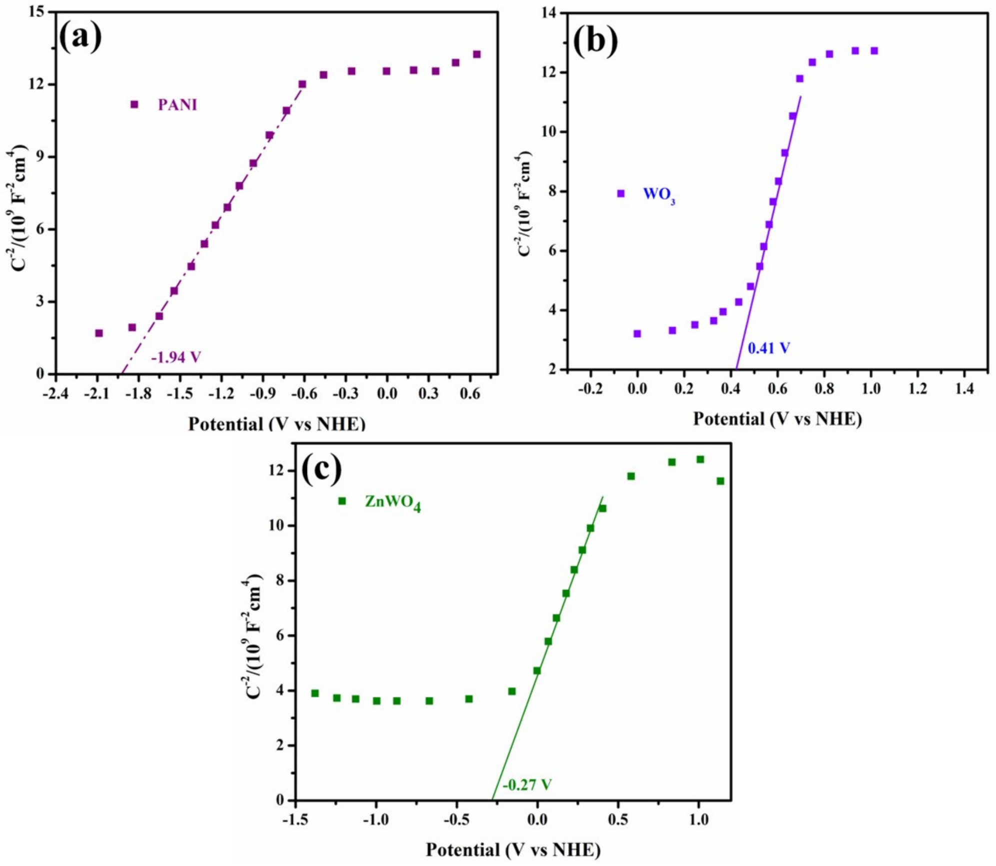

Fig. S6. The Mott-schottky plots of (a)PANI, (b) WO_3, and (c) $ZnWO_4$.

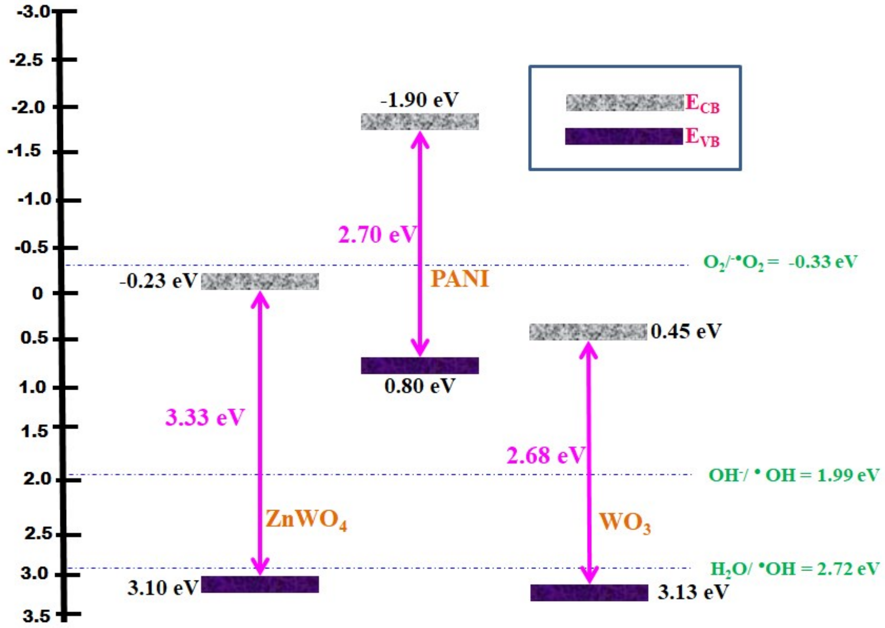

Fig. S7. The band structures of PZW.

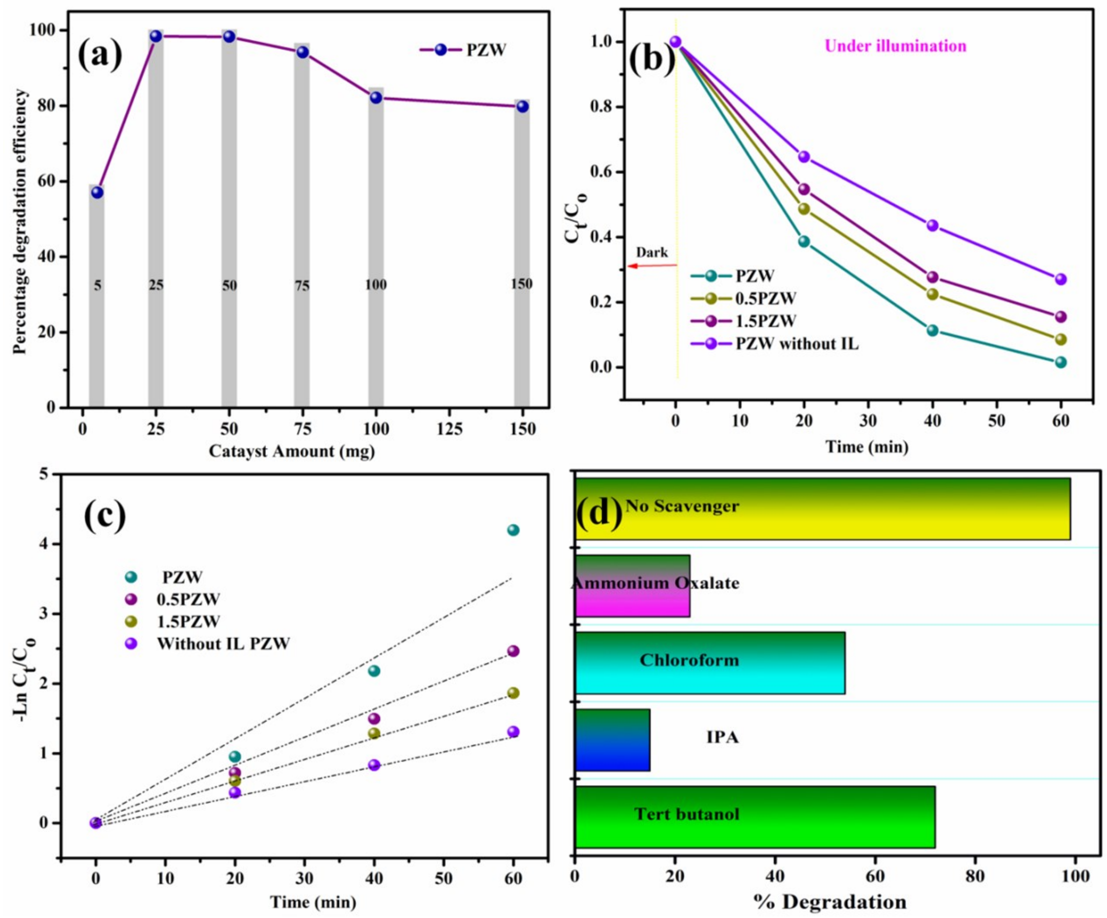

Fig. S8. (a) PZW Photocatalyst amount variation for degradation of 10 ppm GLP solution (100 ml) (b) Photocatalytic degradation of GLP and (c) Pseudo first order kinetic plots for PZW, 0.5PZW, 1.5PZW and PZW synthesized without IL, (d) Radical trapping experiment with PZW nanocomposite.

Conventional Type-II electron transfer mechanism

Under the illumination of sunlight, the electrons in the valence band of $ZnWO_4$, PANI, and WO_3 are excited to their respective conduction bands leaving the photo-generated holes (h^+) behind. If the ternary composite follows type-II mechanism, the holes (h^+) in the higher positive E_{VB} of $ZnWO_4$ and WO_3 migrate to the E_{VB} of PANI. On the other hand, the electrons (e-) migrate in reverse direction to the CB of $ZnWO_4$ and WO_3. From Fig. S9, the conduction band edge of $ZnWO_4$ and WO_3 located at -0.23 and 0.45 eV which is insufficient to reduce O_2 into $O_2^{\bullet-}$ [E_0 (O_2/ $O_2^{\bullet}$) = -0.33 eV vs. NHE]. Again, the photo-generated holes on the valence band of $ZnWO_4$ and WO_3 can't lead to formation of $HO^{\bullet}$ from the HO^- ions/H_2O molecules [E_0 (HO^-/ $HO^{\bullet}$) = 1.99 eV vs. NHE, E_0 ($H_2O/HO^{\bullet}$) =1.99 eV vs. NHE]. This clearly banishes the formation $O_2^{\bullet-}$ from O_2 and the $HO^{\bullet}$ from the HO^- ions/ H_2O molecules. But the radical trapping test and reactive oxygen species quantification have already confirmed $O_2^{\bullet-}$ and $HO^{\bullet}$ as the major active species behind the photocatalytic degradation. So, the possibility of type-II mechanism has ruled out. These results were also supported by MS analysis.

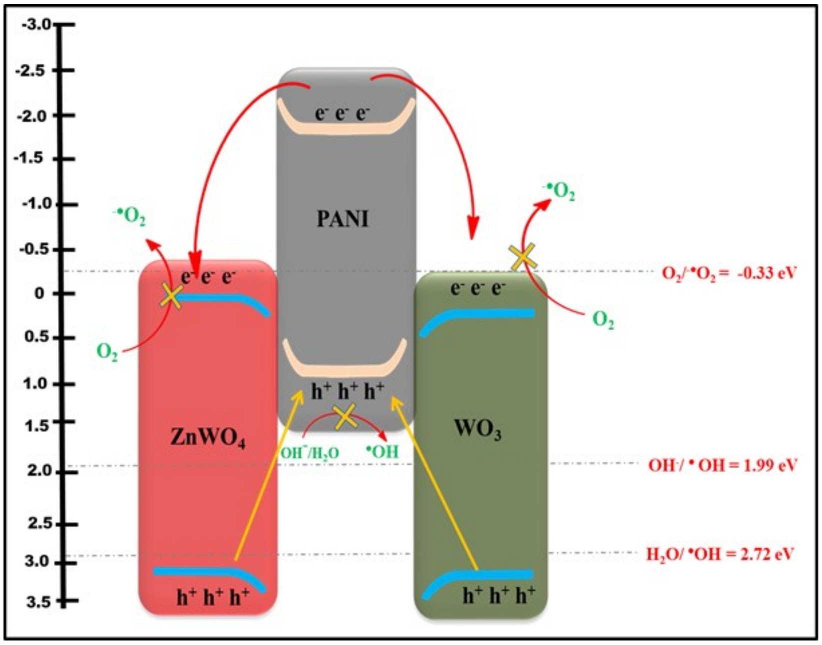

Fig. S9. Conventional Type-II electron transfer mechanism.

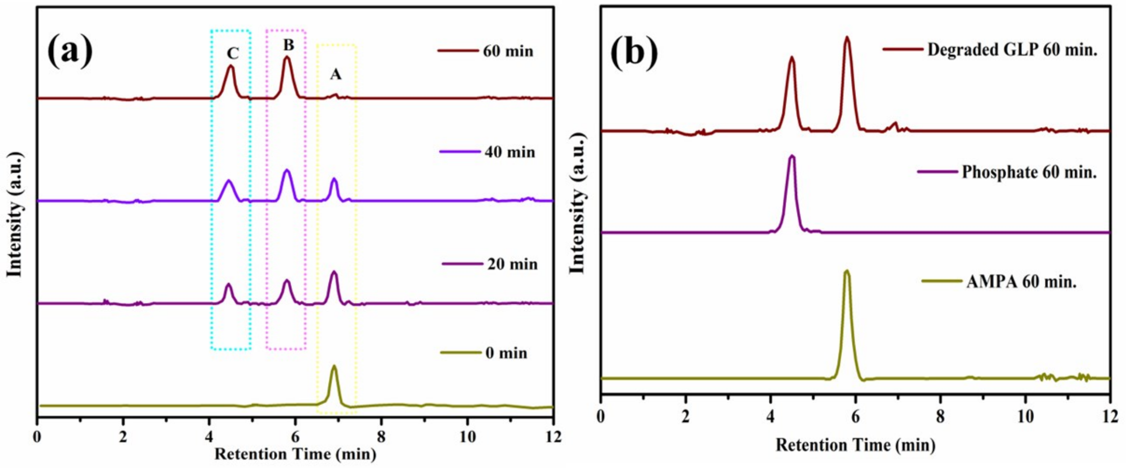

Fig. S10. (a) Typical IC profiles of GLP degradation after different time intervalwhere the peaks are assigned as GLP (A), orthophosphate (B), AMPA (C), (b) IC profiles of AMPA, phosphate, and after photo-treated or degraded GLP.

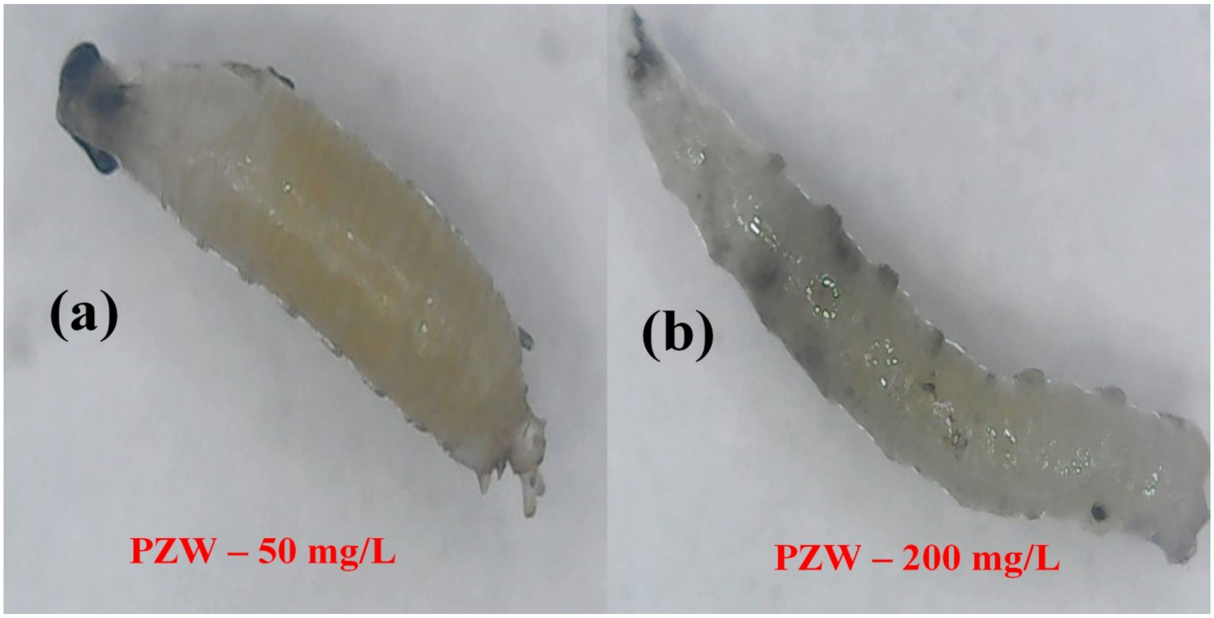

Fig. S11. The unaffected larvae after photo-treatment with 50mg and 200mg of PZW photocatalyst.

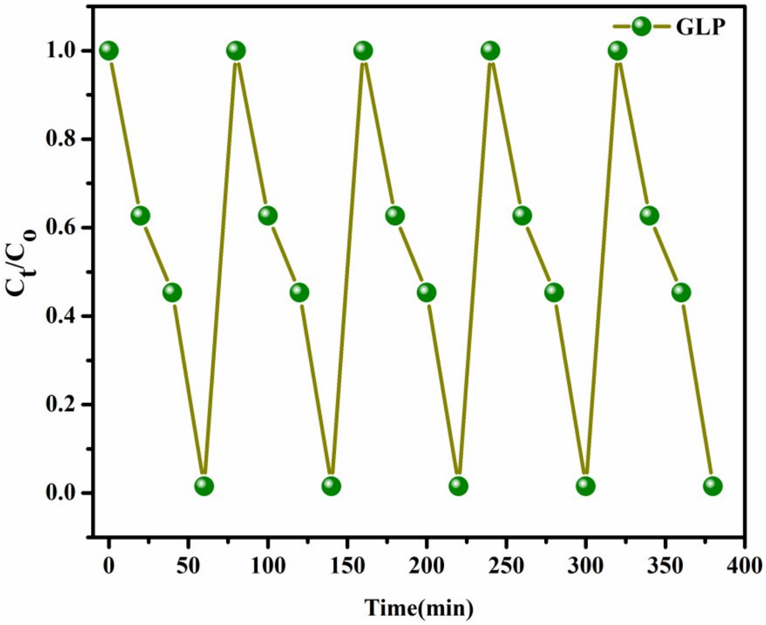

Fig. S12. Reusability of PZW photocatalyst after five continuous cycles.