

Electronic Supplementary Information

Electron trapping protocol of FePW₁₂O₄₀ microflowers with dual catalytic Properties: Visible light photodegradation of amphetamine and electrocatalytic oxygen evolution

Characterization

Various analytical techniques have been utilized to investigate the morphological and electronic properties of the developed FePW₁₂O₄₀ samples. The X-Ray diffractogram have been obtained from a Bruker analytical diffractometer. The radiation was obtained from a Cu-K α source at 40 kV and 30 mA with a scanning range from 10° to 60°. A field electron scanning electron microscope (FESEM-ZEOL) was used to obtain images of the surface morphology of the prepared sample. The particle structure and orientation was further investigated using FEG-TEM. Photoluminescence (PL) spectrum of the sample was recorded on a Hamamatsu R928 photomultiplier detector with He–Cd laser as the excitation source operating at 325 nm with an output power of 50 mW. The optical absorbance of the sample was recorded using a LAMBDA 25 UV/vis spectrophotometer (Perkin Elmer, India). A thermogravimetric (TG) analyzer (TGA-Q50, TA instruments, USA) is used to measure the weight loss% with increasing temperature under inert (nitrogen) atmosphere with a heating rate of 10⁰C/min in a vertical type pan, automated sampling chamber. X-ray photoelectron spectroscopy (XPS, ULVAC PHI 5000 versaprobe II, Japan) with Al K α electrode was used to analyze Valence band X-ray photoelectron spectroscopy (VB-XPS) spectrum to see the feature of material valence band. Fourier Transform Infrared Spectroscopy (FTIR, PerkinElmer, India) was used to identify the fundamental molecular vibration in the material. EPR spectroscopy were accomplished by a Bruker (Model No.: ELEXSYS 580) pulsed electron paramagnetic resonance spectrometer with the microwave X-band frequency range of 8-12 GHz at room temperature. Electrochemical impedance spectroscopy (VersaStat-3, Princeton Applied Research, USA) were introduced to observe the charge transfer flexibility of photogenerated electron.

Photocatalytic experiment setup

The photocatalytic activity of the synthesized samples was tested by degradation of a 20 ppm solution of pharmaceutical drug amphetamine. The degradation test was carried out in a 500 ml cylindrical glass reactor with 0.05 g of the prepared catalysts dispersed in it. The reactor had a centrally pivoted quartz tube which was equipped with a CFL lamp ($\lambda > 400$ nm, Philips, India with a cutoff filter). An air supply of 0.5 LPM from a vacuum pump ensured continuous agitation of the reaction mixture in the annular space. Initially, the reaction was allowed to take place with the light source turned off. This was carried out for 2 hours to achieve adsorption desorption equilibrium. Then light was turned on and

photocatalytic degradation commenced. A 5 ml sample was collected at every interval of 15 minutes followed by separation of the catalysts by centrifuging at 8000 rpm. A UV-vis spectrophotometer was then used to check the absorbance of the samples. Then the concentrations of the samples were determined from a previously prepared absorbance vs concentration calibration curve.

Photoelectrochemical studies

A conventional three electrode cell was used to conduct photoelectrochemical experiments. The working electrodes were prepared by initially ultrasonically dispersing a 30 mg catalyst sample in a solution of 9 ml ethanol and 1 ml nafion. Then the solution droplets were dispensed on an ITO glass cell with 1 cm² surface area, followed by drying. Thus the working electrodes were prepared. An Ag/AgCl electrode was chosen as reference electrode and Pt wire was used as counter electrode. A 300 W Xenon lamp with $\lambda > 400$ nm cut-off filter served as the light source. A 1.0 M KOH solution was used as electrolyte and measurements were taken by a CHI643B electrochemical workstation connected to the photoelectrochemical cell.

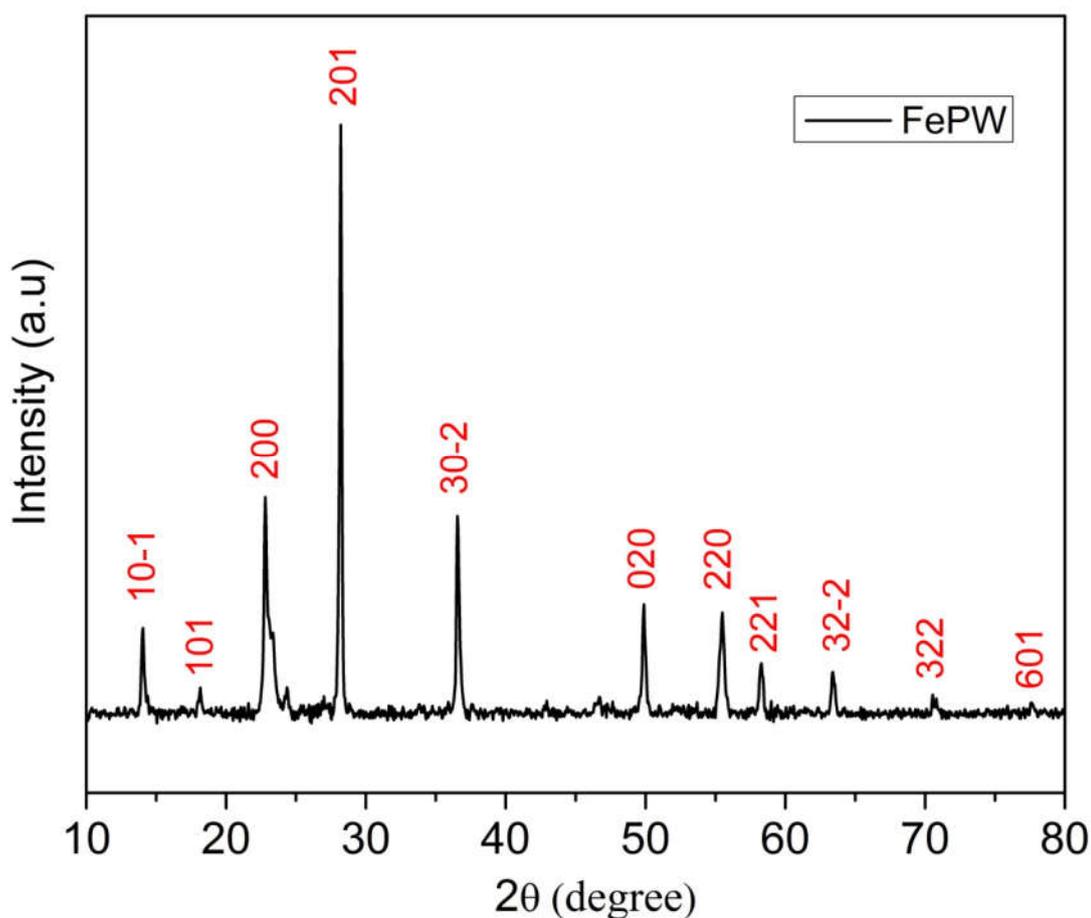


Fig. S1: Powder XRD pattern of FePW

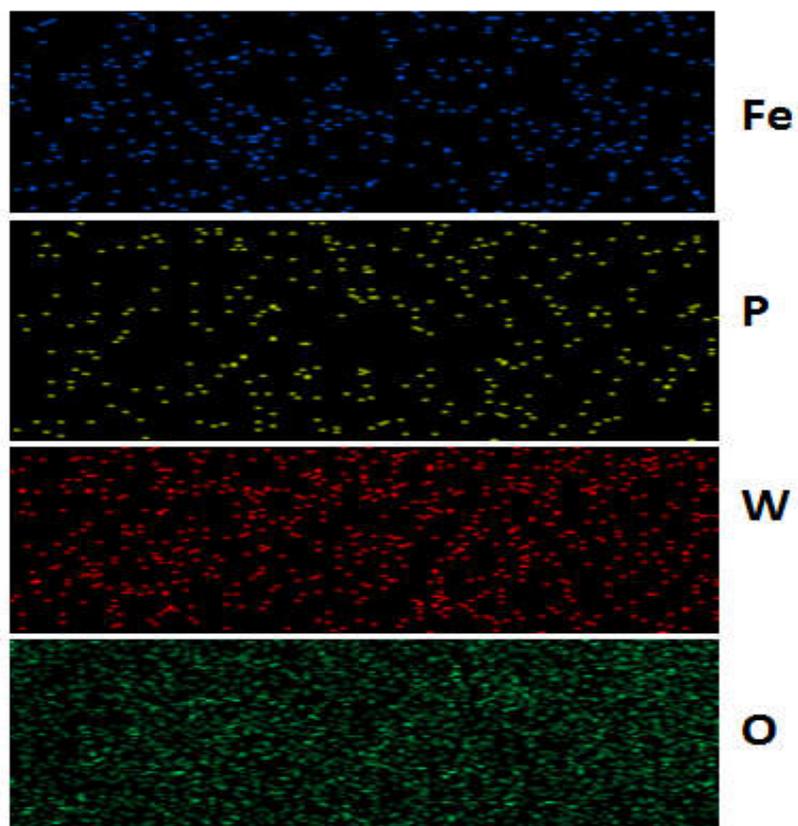


Fig. S2: EDX pattern of Fe, P, W, O in FePW

Thermogravimetric studies were conducted on the synthesized FePW samples to estimate their thermal stability. A slight weight loss of 6.8% up to 350 °C was observed, as presented in Fig. S3a, ESI.† This can be attributed to removal of adsorbed water molecules. There is no weight loss at a higher temperature range of 300–700 °C, thus revealing the thermal stability of the polyoxometalate photocatalyst.

The FTIR spectra of the synthesized FePW sample was recorded at a range of 450–5000 cm^{-1} to identify the chemical bonds present, and to analyze their nature. The bands at 3420 cm^{-1} and 1621 cm^{-1} represent the stretching and bending vibration modes of OH groups respectively, as shown in Fig. S3b, ESI.† The bands between 1100 and 750 cm^{-1} represent characteristic bonds in the Keggin structure of polyoxometalates. The narrow band at 962 cm^{-1} represents asymmetric stretching vibration of the $W-O_d$ bond where O_d represents the terminal oxygen atom, while the band at 1078 cm^{-1} represents the asymmetric stretching vibration of the $P-O_a$ bond in the PO_4 tetrahedron. The bands at 815 cm^{-1} and 755 cm^{-1} represent the asymmetric stretching vibrations due to the bridge oxygen atoms in the $W-O_c$ and $W-O_b$ bonds.¹ The broad band at 585 cm^{-1} arises due to the stretching vibration of a Fe–O bond.² Thus the development of a polyoxometalate complex linked to Fe atoms is confirmed.

The photocatalytic response was enlightened by dissolving 1 mM solution of scavengers including EDTA, $AgNO_3$ and tertbutyl alcohol (TBA), which could trap photo-induced holes (h^+), photo-induced electrons and OH radicals, respectively (Fig. S7a, ESI†). A neurotoxic drug, amphetamine was selected as the target pollutant. It is observed that the degradation efficiency decreases with the addition of tert-butyl alcohol (TBA) and EDTA and increases with the addition of $AgNO_3$, confirming the key role of OH and h^+ in this reaction. Electron, hole and OH radical trapping in the experiment clearly depicts the involvement of photogenerated free radicals in the reaction.

The photocatalytic properties of the synthesized POM can be further validated by the disappearance of peaks in the absence of light due to no charge carrier generation. Upon application of visible light, holes are formed in the valence band of the photocatalyst, which react with OH^- ions to OH radicals. These OH radicals have a very high oxidation potential of 1.7–2.7 eV^3 and are mainly responsible for the oxidative degradation of amphetamine. A possible degradation pathway of amphetamine is presented in Fig. S10, ESI,† and its explanation is provided in the ESI.†

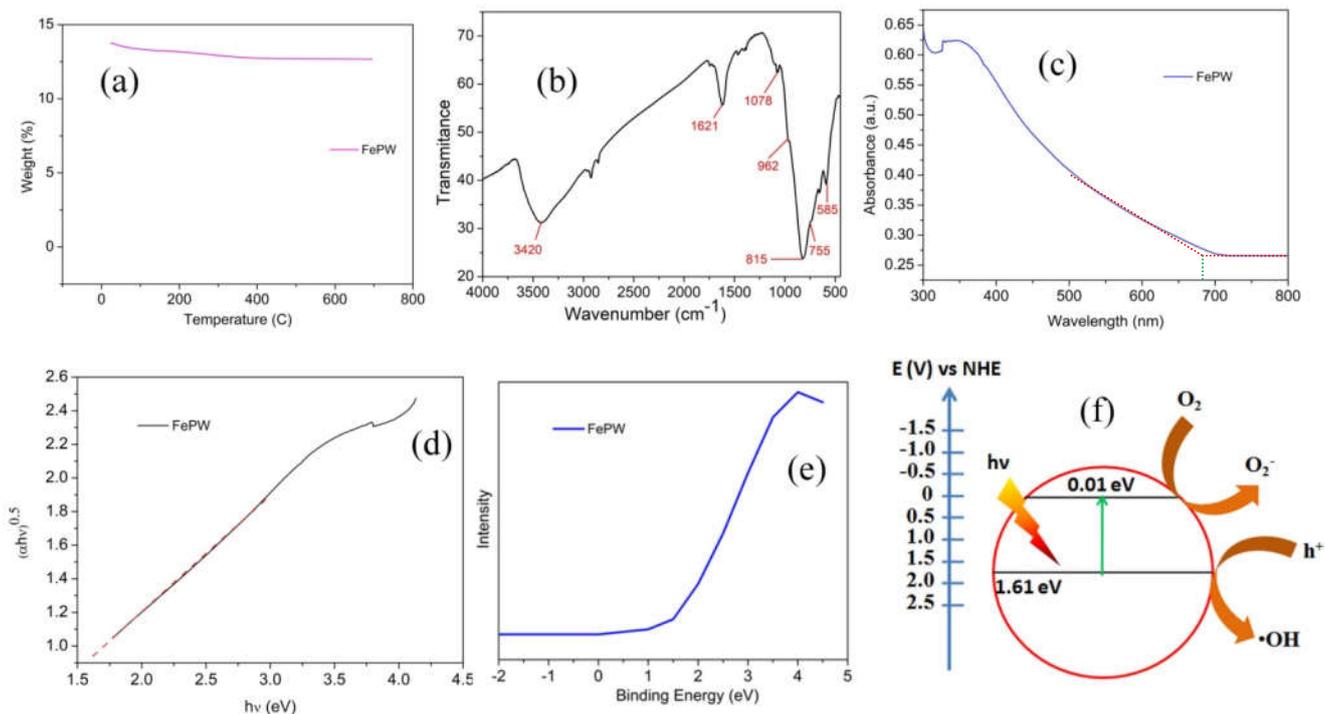
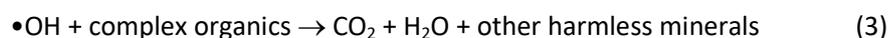
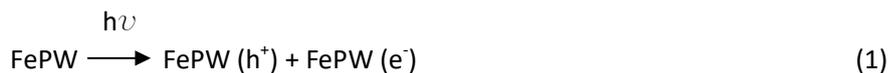


Fig. S3: a. Thermogravimetry of FePW, b. FTIR spectrum, c. UV-vis absorbance spectrum, d. Tauc plot for FePW, e. VB XPS analysis, f. Band diagram of FePW

Upon incidence of visible light, localization of electrons and holes takes place on the O and W, Fe atoms respectively, as shown in Eqn. 2,3 in the main manuscript. These positively charged holes react with OH⁻ ions in solution to form the highly oxidative •OH radicals. These •OH radicals degrade complex organic pollutants to harmless minerals. The VB electrons may be trapped by atomic level defects serving as electron traps, or they react with O₂ molecules in solution to generate superoxide anions (O₂⁻). The equations have been presented accordingly:



The degradation pathway of complex organic amphptemaine by $\text{OH}\bullet$ radicals has been presented in Fig. S10 and discussed in the main manuscript.

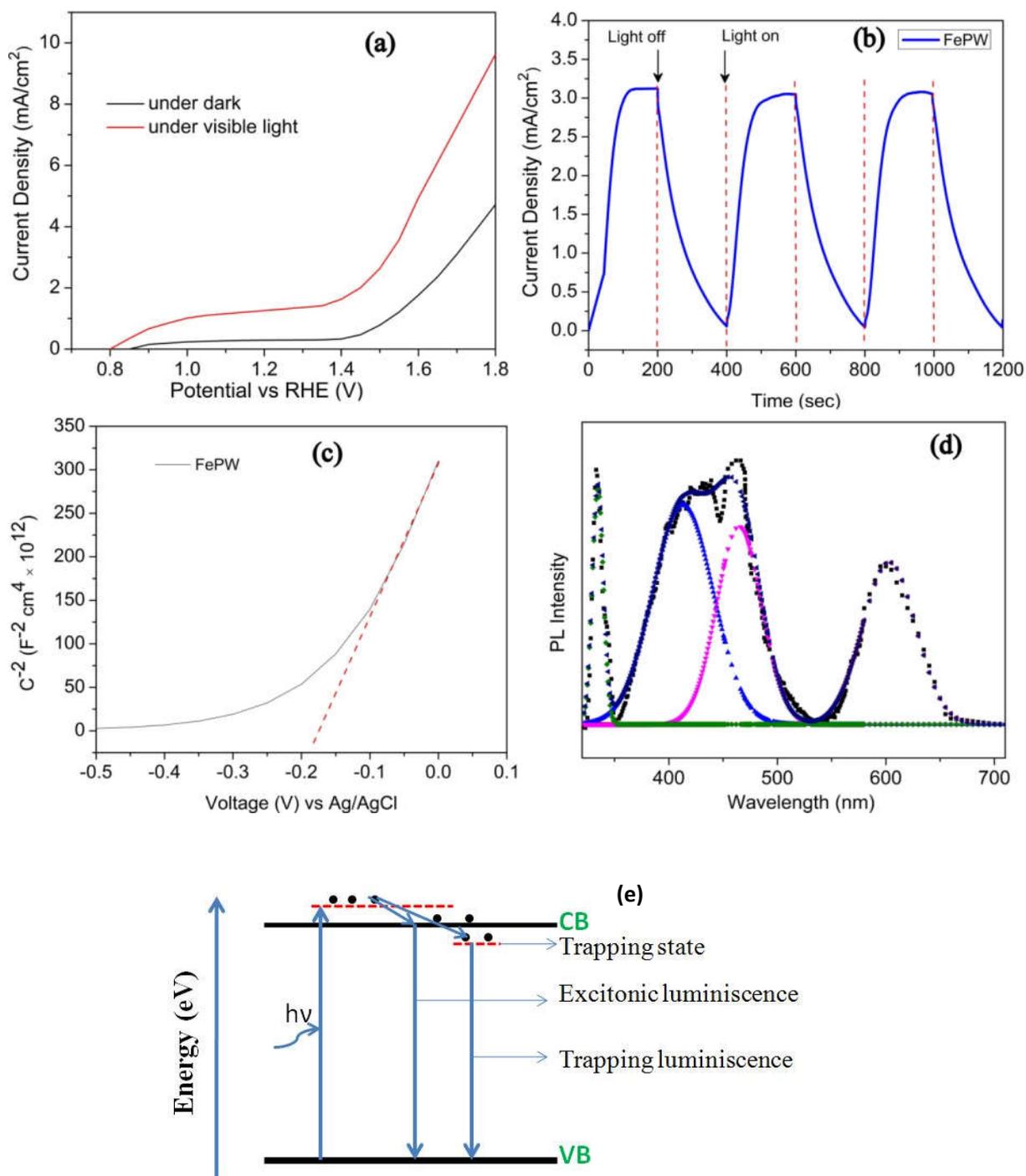


Fig. S4: a. Cyclic voltammety of FePW, b. Transient photocurrent response, c. Mott-schottky analysis, d. PL spectrum of FePW e. Schematic of trapping luminescence

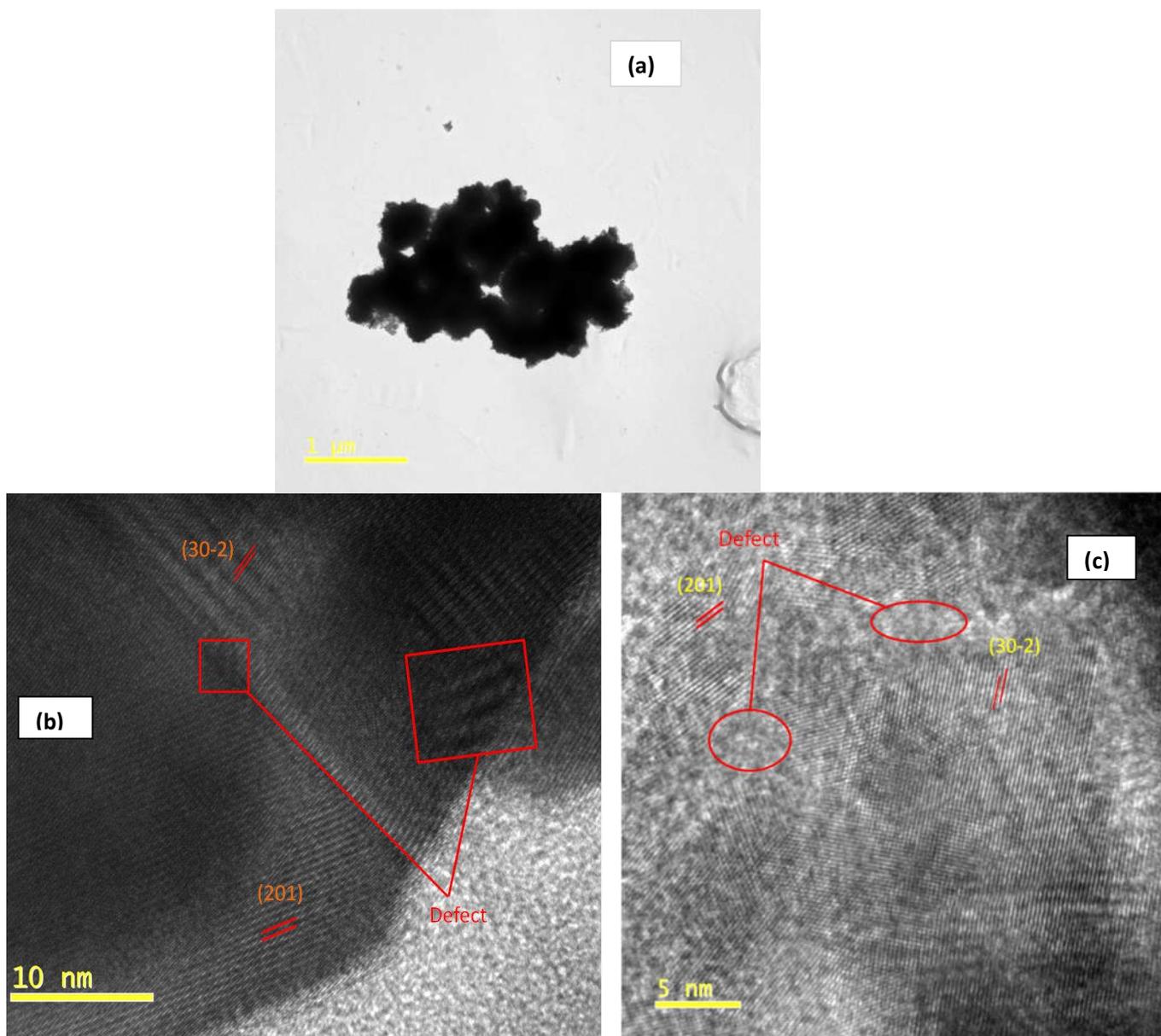


Fig. S5: (a) Low Magnification HRTEM image of FePW microflowers (b) and (c) Lattice fringe study in high magnification HRTEM images

The microflowers are clearly visible in Low magnification HRTEM images, as shown in Fig. S5a. High magnification HRTEM images of the FePW samples have been collected to develop further insights on

atomic level structures and their distortions. In the images presented in Fig. S5(b-c), lattice fringes corresponding to (30-2) and (201) facets can be easily indexed based on their d-spacings of 0.31 nm and 0.23 nm respectively. Since top view images reveal (30-2) and (201) facets, we can conclude that the growth of the crystal takes place along their perpendicular axis corresponding to the (020) facet, which was identified in the XRD analysis. We can further identify some structural distortions as marked by red, in the HRTEM images. These discontinuities and dark spots in the well ordered fringes can be attributed to the presence of atomic level defects, which serve as electron traps as discussed in the PL spectra and Fig.2 in the main manuscript.

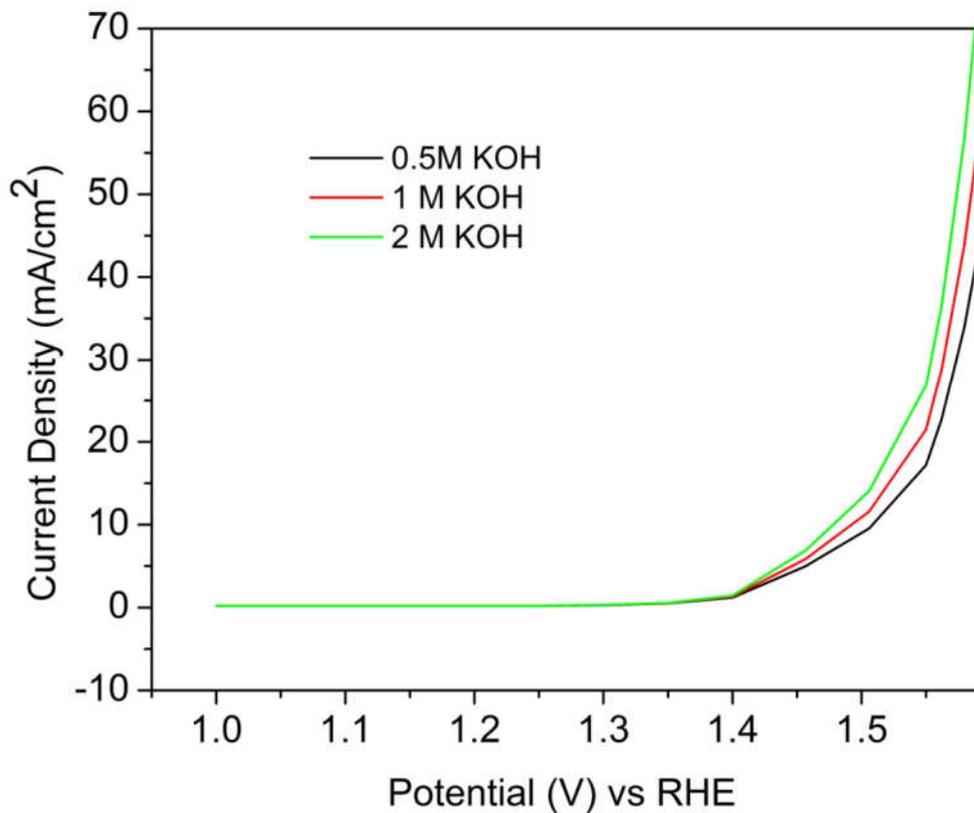


Fig S6: LSV polarization plot at different KOH concentration

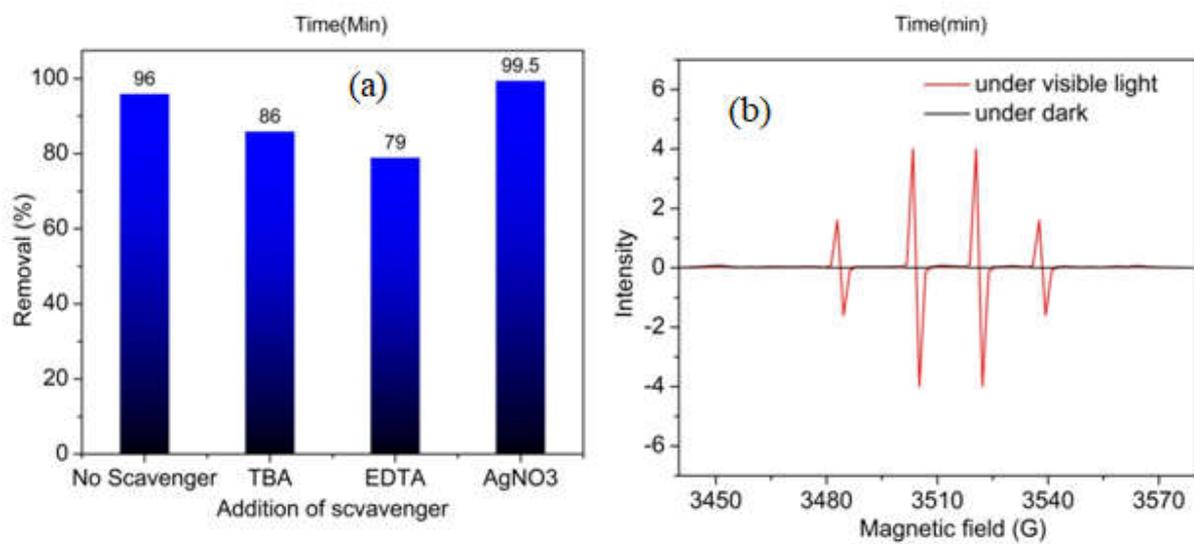


Fig. S7: a. Trapping experiment, b. EPR analysis of FePW

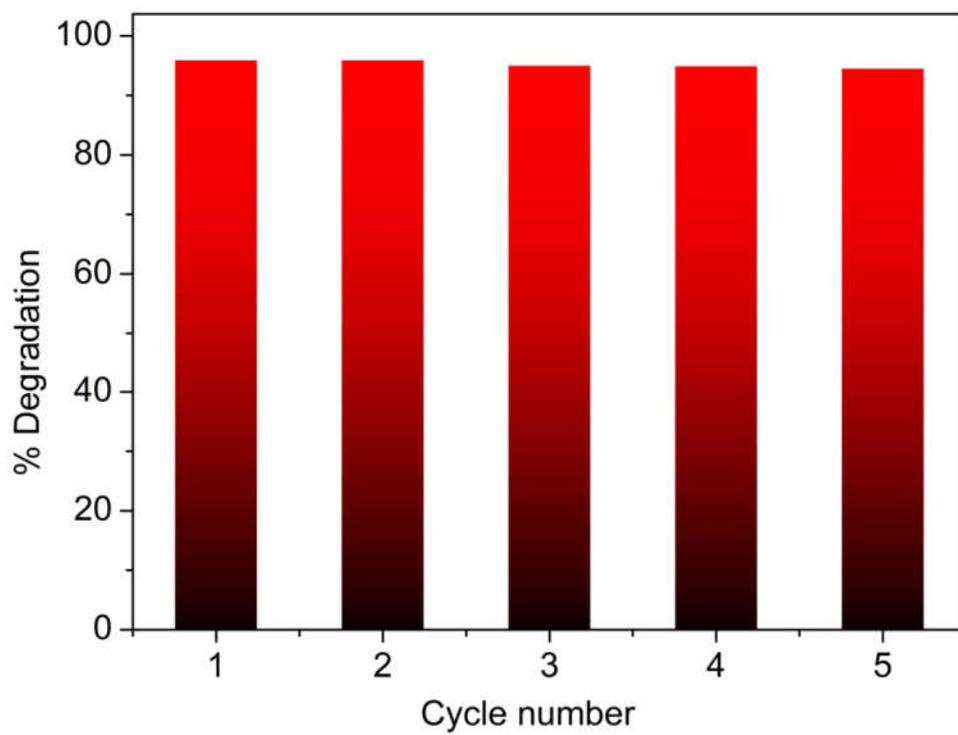


Fig. S8: Photocatalytic stability of FePW for recycle and reuse

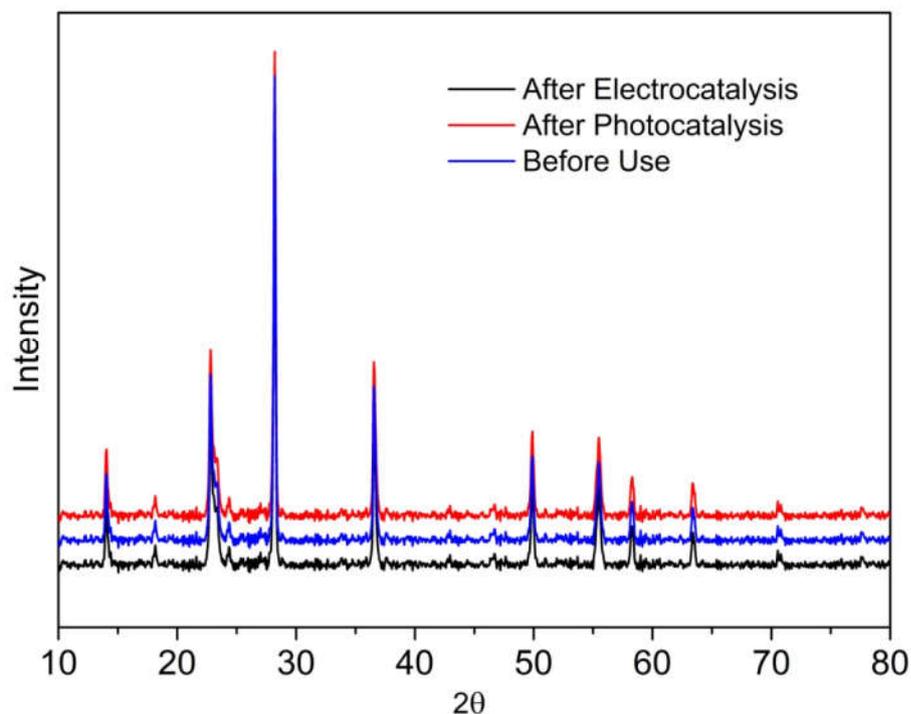


Fig. S9: X-Ray Diffratograms of FePW before and after photocatalytic/electrocatalytic activity

The structural stability of the FePW samples were investigated by obtaining their X-Ray Diffractograms after photocatalytic/electrocatalytic experiments. The FePW coated ITO glass was first sonicated in a beaker to recover the FePW samples in the solution. Then the solution was centrifuged to obtain the FePW samples. Similarly, The solution in the photocatalytic reactor was centrifuged and dried to obtain FePW sample. The X-Ray diffractograms didnt reveal any change post photocatalytic/electrocatalytic treatments, thus establishing excellent structural stability of the polyoxometallate samples.

As depicted in Fig.S10, the $\bullet\text{OH}$ radicals first attack the first C-C bond in the side chain creating a $\text{CH}\bullet$ radical by abstraction of a hydrogen atom. This radical further reacts with $\bullet\text{OH}$ radicals to form 1-phenyl 2-amino propanol. The hydrogen atom is abstracted by more $\bullet\text{OH}$ radicals to form a $\text{CO}\bullet$ radical in the first carbon atom of the side chain. The C-O bond undergoes fast radical reaction followed by cleaving of the amino group to form benzaldehyde and an intermediate free radical $\text{CH}_3\text{CH}\bullet\text{NH}_2$. The highly oxidative $\bullet\text{OH}$ radicals oxidize the benzaldehyde to benzoic acid and finally to CO_2 and H_2O . The free radical containing the amino group reacts with $\bullet\text{OH}$ radicals to form 2-amino propanol, which is further oxidized to acetaldehyde and finally to ammonia, carbon dioxide, and water.

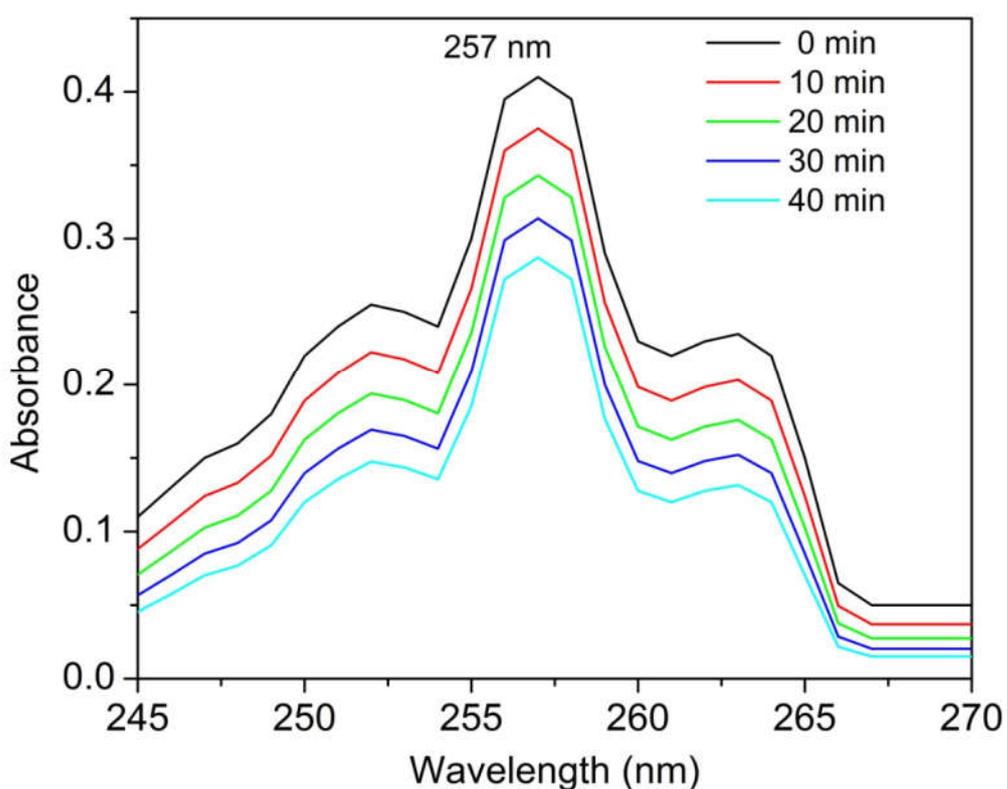


Fig. S11: Photodegradation of amphetamine with time in presence of FePW

Amphetamine degradation was measured by UV-vis spectrometry at maximum wavelength of absorbance 257 nm.

References:

1. C. Rocchiccioli-deltcheff, M. Fournier, R. Franck, and R. Thouvenot, *Inorg. Chem*, 1983, 22, 207–216.
2. A. Bava, F. Cappellini, E. Pedretti, F. Rossi, E. Caruso, E. Vismara and M. Chiriva-Internati, *BioMed Research International*, 2013, 1–10
3. G. Buxton, C. Greenstock, P. Helman and A. Ross, *J. Phys. Chem*, 1988, 17, 513–886.