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Supplementary Information

MOF derived-Mn₂O₃ decorated MoS₂-graphene composite for visible light assisted degradation of environmentally hazardous penicillin G in water

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Instrumentation

Powdered X-ray Diffraction (PXRD) was measured by Bruker APEX-2 diffractometer. Fourier Transform Infra Red spectra (FT-IR) were carried out with a Perkin-Elmer FT-IR spectrophotometer RXI. The X-ray Photoelectron Spectroscopy (XPS) was performed by Specs (German). Thermogravimetric Analysis (TGA) was analysed on Perkin-Elmer instrument, Pyris Diamond TG/DTA with Al₂O₃ crucible. Transmission Electron Microscopy (TEM) and High Resolution TEM (HRTEM) were performed with JEOL JEM2010 electron microscope operating at 200 kV. Energy Dispersive X-ray (EDX) measurement was carried out with FEI TECNAI-G2-20S-TWIN (USA). BET surface area and N₂ sorption isotherms (77K) were carried out by Quantachrome Autosorb-1 instrument. Photoluminescence spectra were recorded by F-7000 FL Spectrophotometer. The photodegradation of PG were measured by UV- 1601, Shimadzu spectrophotometer and high performance liquid chromatography (HPLC, Thermo Fisher Scientific Dionex UltiMate 3000). Photo-electrochemical analyses, such as photocurrent (LSV) and EIS were measured by a potentiostat (Versa STAT 3, Princeton Research, USA) consisted of a standard three-electrode system. Ag/AgCl (3 M KCl) was used as the reference electrode and Pt gauge was used as the counter electrode, and fluorine doped-tin oxide (FTO) glasses coated with the MSG, pure Mn_2O_3 and MMG-3 composites were used as the working electrodes. The working electrode was prepared by doctor-blade method¹. In each case, 0.2 M aqueous sodium sulphate solution has been used as the supporting electrolyte. The photocurrent response was measured at a scan rate of 50 mV s⁻¹ over the potential range -1.0 to 1.0 V. The electrochemical response was recorded under light irradiation ($\lambda > 420$ nm, 300 W Xe lamp with a UV-cutoff filter).

1. J. Power Sources, 195 (2010) 7078-7082.



Fig. S1 a) FT-IR spectrum, b) PXRD pattern and c) TGA of the synthesized Mn-MOF.

The CO stretching frequency shifted from 1686 cm⁻¹ for the un-coordinated ligand 1,4- H_2BDC to 1564 cm⁻¹ after the coordination with Mn²⁺ ions.¹ A strong and broad peak at around 3384 cm⁻¹ is due to H_2O molecules with hydrogen bonds, which participates in the coordination of Mn⁺² in the Mn-MOF structures. The peak at 1386 cm⁻¹ in the MOF is for carboxylate stretching frequencies of the ligand, BDC²⁻.

The PXRD of the MOF reveals sharp intense peaks indicating its crystalline nature.

TGA shows a minor weight loss at around 150-175 °C due to loss of water molecules from the MOFs, and a major weight loss (~70 %) at around 350 °C due to presence of terephthalate ligands in the Mn-MOF. Hence, the MOF was heated at 400 °C for their transformation to corresponding Mn_2O_3 .

1. M. Rakibuddin, R. Ananthakrishnan, RSC Adv. 5 (2015) 68117-68127.



Fig. S2 a) Diffuse reflectance spectrum and b) Tauc plot for determination of band gap of the pure MSG.

The band gap of the pure MSG sample is calculated to be 1.75 eV.



Fig. S3 SAED pattern of the Mn_2O_3 , MSG and MMG hybrid.



Fig. S4 TGA of the MMG-3, MMG-5 hybrid and Mn_2O_3

The weight loss in the TGA profile indicates the presence of 3% and 5% MSG in the MMG-3 and MMG-5 hyrid, respectively.



Fig. S5 UV-Visible absorption spectra (200 to 800 nm) for the degradation of PG under visible light in presence of MMG-3.



Fig. S6 HPLC Chromatogram for the degradation of PG at different time intervals under visible light in presence of MMG-3 composite.

HPLC chromatogram indicates degradation of PG with time under visible light in presence of the catalyst. The HPLC were consisted of a UV/Vis Diode Array Detector and a reversed-phase Acclaim Polar Advantage-II column (3 μ m, 120 A°, 3 ×150 mm). The chromatographic conditions were: 80: 20 for mobile phase (V) acetonitrile: water, 0.3 mL min⁻¹ for the flow rate of mobile phase, 20 μ L for the injection volume, 30 °C for column temperature and the detection wavelengths for PG was 325 nm.

From the HPLC analysis, a sharp chromatogram peak of PG is observed at the retention time of 3.5 min, which is gradually decreased with time indicating gradual degradation of the PG as supported by the UV-Vis spectra. No other products are found in the chromatogram which suggests direct mineralization of PG into CO_2 and water by the MMG-3 composite.



Fig.S7 PL spectra of the MMG-3 hybrid and Mn_2O_3 .