Electronic Supplementary Information

Enhanced Z-scheme Photocatalytic Activity of Conjugated ∏ Heterojunction: MIL-53(Fe)/Ag/g-C_3N_4

Sovan Kumar Patra‡, Sibsankar Rahut‡, Jayanta Kumar Basu*
Department of Chemical Engineering, Indian Institute of Technology, Kharagpur-721302, India

Email: **jkb@che.iitkgp.ernet.in**

Characterization

Powder X-ray diffraction studies (PXRD) were carried out on a Bruker D8 Advance diffractometer with a step size of 0.02^{o} and a scan speed of 0.5 second per step in the 2θ range of 10^{o} to 70^{o}. The Fourier transform infrared (FTIR) spectroscopy of the samples were conducted on Perkin Elmer Spectrum 100 instrument in the range of 400-4000 cm. KBr was used as a binder to make pallet for all samples. A Perkin Elmer lambda 25 spectrophotometer was used to measure the optical absorbance spectrum of all samples. It was also used to calculate the concentration of CLQ by measuring absorbance at λ = 268 nm. Photoluminescence (PL) estimations were carried out with a He-Cd laser as the excitation source working at 325 nm and harvest energy of 50 mW. A TRIAX-320 monochromator was utilized to transmit chosen wavelengths of light and the Hamamatsu R928 photomultiplier detector was utilized to catch signals in the visible range. The surface morphology was scrutinized by Field Electron Scanning Electron Microscope (FESEM-JEOL, Japan). Exact nanodispersion and particle sizes were determined by High Resolution Transmission Electron Microscope image (HR-TEM) that was captured by JEM-2100 HRTEM (JEOL, Japan) with a direct resolution of 0.194 nm and a grid resolution of 0.14 nm. Energy dispersive X-ray (EDX) spectroscopy (Oxford, UK) was used to analyze atomic mapping. BET surface area was measured by using a Quantrachrome AUTOSORB iQ instrument by adsorption of nitrogen at 77K on 200 mg of sample previously degassed at 200^{o}C under vacuum.X-ray photoelectron spectroscopy (XPS, ULVAC PHI 5000 versa probe II, Japan) with Al Kα electrode was used to analyze the binding and electronic state of designed sample.

Photo-electrochemical studies

A conventional three electrode cell was used for photo-electrochemical studies. A 30 mg sample was sonicated with 9 mL ethanol, 1 mL Nafion. An ITO glass cell with an exposure of 1 cm^2 area was used as a spin-coated sample to fabricate a working electrode. Ag/AgCl as the reference electrode and a Pt wire as the counter electrode were connected to the CHI643B electrochemical workstation using 1.0 M sodium nitroprusside solution as electrolyte. A 300 W Xe light outfitted with a cutoff channel (λ > 400 nm) was utilized as the illumination source.

Electrochemical studies

A similar three-electrode system was used for electrochemical characterization without using any light source. The linear sweep voltammetry was conducted at a scan rate of 100 mV s^{-1} with different concentrations of the KOH solution (0.1–2 M) as the electrolyte. The solution resistance was calculated by impedance spectroscopy.

Computational methodology

Configuration integral singlet (CIS) calculation discloses the excitation state and electronic transition of the molecule. An *ab initio*, DFT and semi-empirical electronic structure package[1] was also introduced to calculate the energy and oscillation strength of each excitation state. SCF-MO package, ORCA are used to calculate molecular electronic structures. Excited states are calculated via CI-singles (CIS) with the semi-empirical Hamiltonian ZINDO.

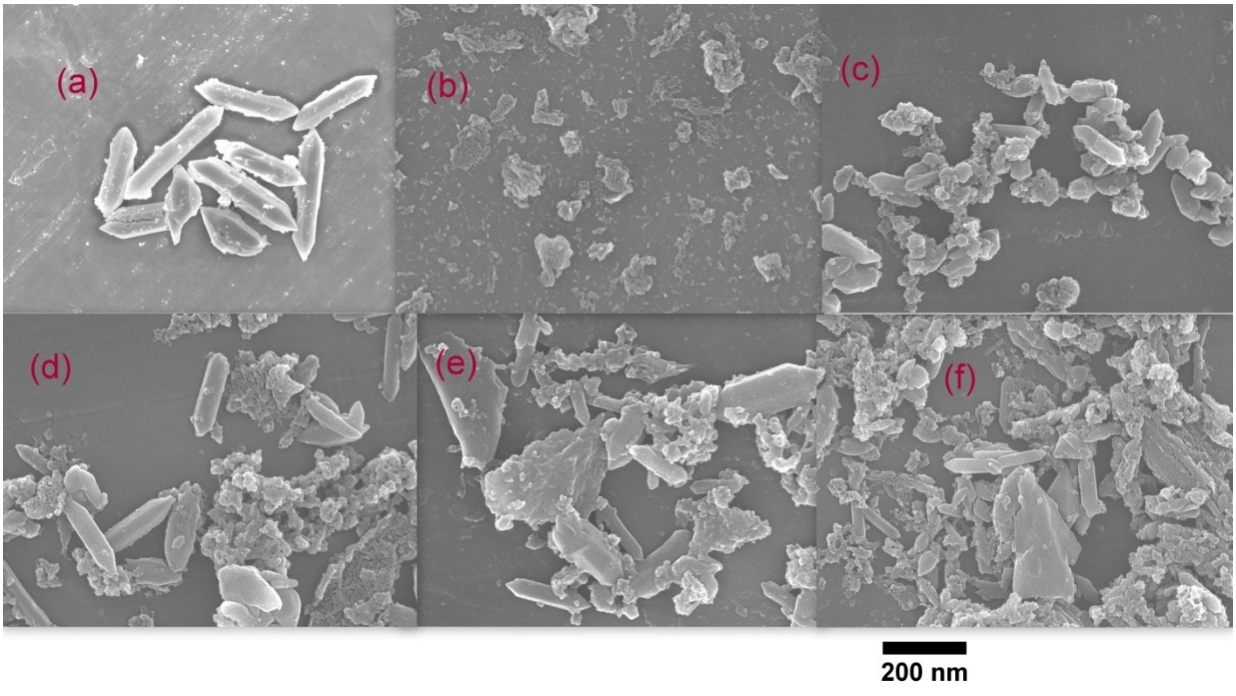


Fig. S1: a. FESEM micrograph of MIL-53 (Fe), b. FESEM micrograph of Ag/g-C_3N_4, c. FESEM micrograph of MACN 20, d. FESEM micrograph of MACN 50, e. FESEM micrograph of MACN 80, f. FESEM micrograph of MACN 100.

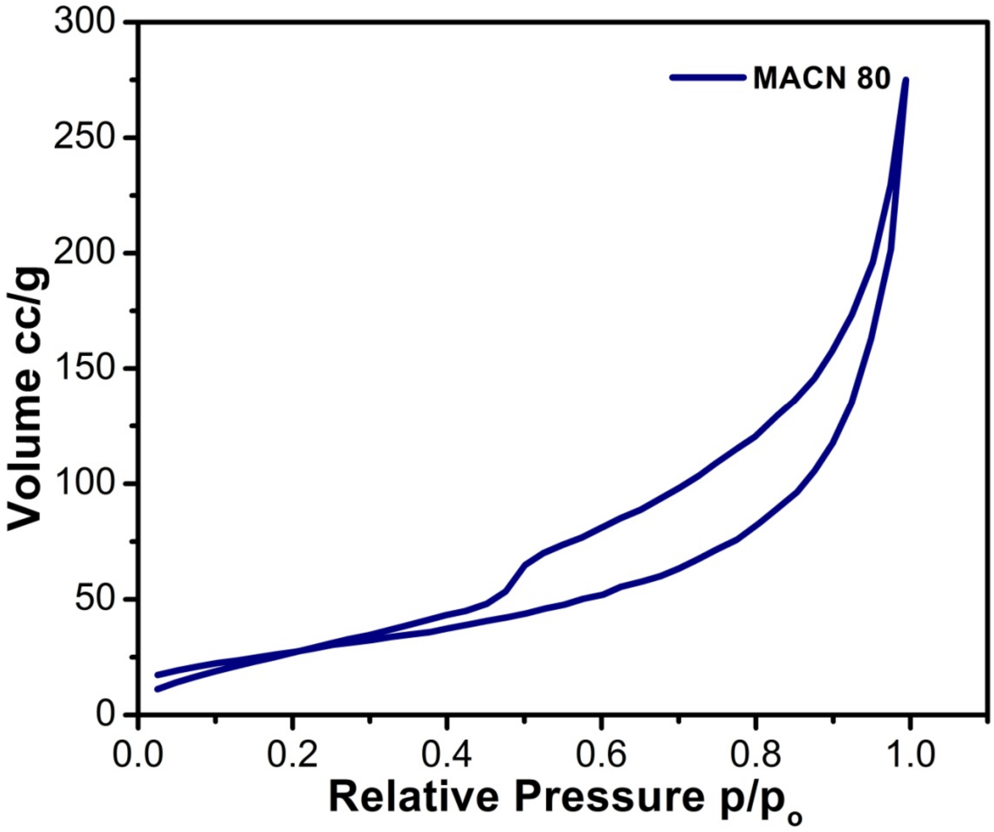


Fig. S2: BET adsorption isotherm

Table S1: BET surface area of Designed sample

S. No	Sample Name	Surface Area (m^2/g)	Pore Volume (cm^3/g)
1	Ag/g-C_3N_4	127.940	0.506
2	MACN 80	114.096	0.334
3	MACN 50	100.425	0.367
4	MACN 20	96.281	0.370
5	MIL-53 Fe	95.262	0.353

External surface area, total pore volume and average pore diameter MIL-53 (Fe), g-C_3N_4, Ag/g-C_3N_4, MACN 20, MACN 50, MACN 80 are shown in table S1. It is found that the BET surface area of MACN 80 significantly improved on addition of different wt. ratios of Ag/g-C_3N_4. Ad sorption characteristics were examined by N_2 adsorption and desorption isotherms (Figure S2), it shows that MACN display identical curves as that of type IV isotherm, which indicate the presence of mesoporous and microporous materials[2].

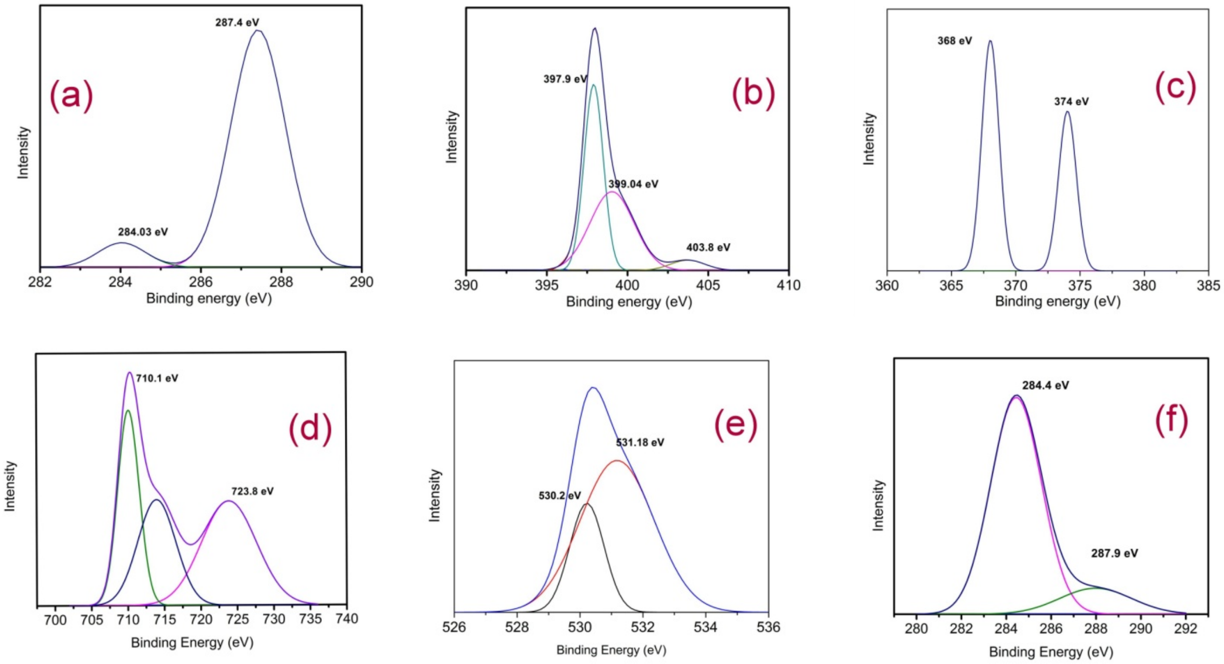


Fig. S3: XPS survey of C 1s spectrum (a), N 1s spectrum (b) and Ag 3d spectrum (c) in Ag/g-C_3N_4, XPS survey of Fe 2p spectrum (d), O 1s spectrum (e) and C 1s spectrum (f) in MIL-53(Fe).

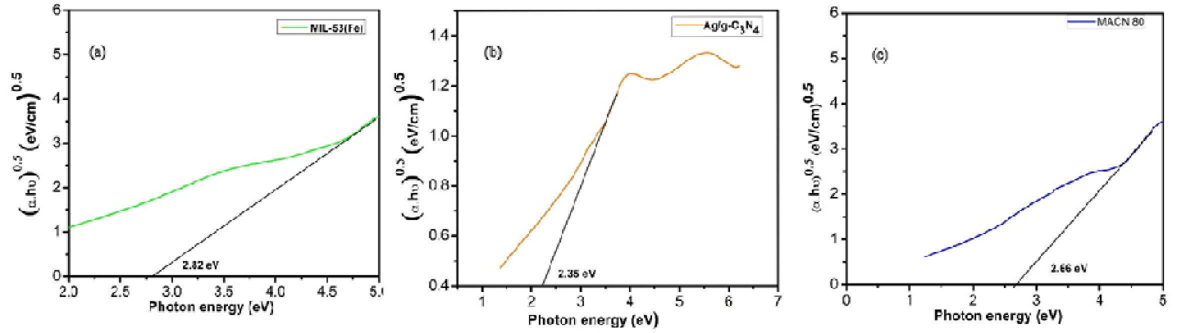


Fig. S4: Tauc plot

Synthesis of Ag/g-C_3N_4: At first g-$C_3N_4$is prepared as mention above. Then 1, 3, 5, 7% by weight of Silver Nitrate solution was added to g-C_3N_4, followed by ultrasonication and then the obtained sample was annealed in muffle furnace at 400 ^{0}C for 4 hr. The resulting whitish-yellow powder was collected and used for further analysis. Based on the wt% samples are designated as Ag-1, Ag-3, Ag-5, Ag-7 respectively.

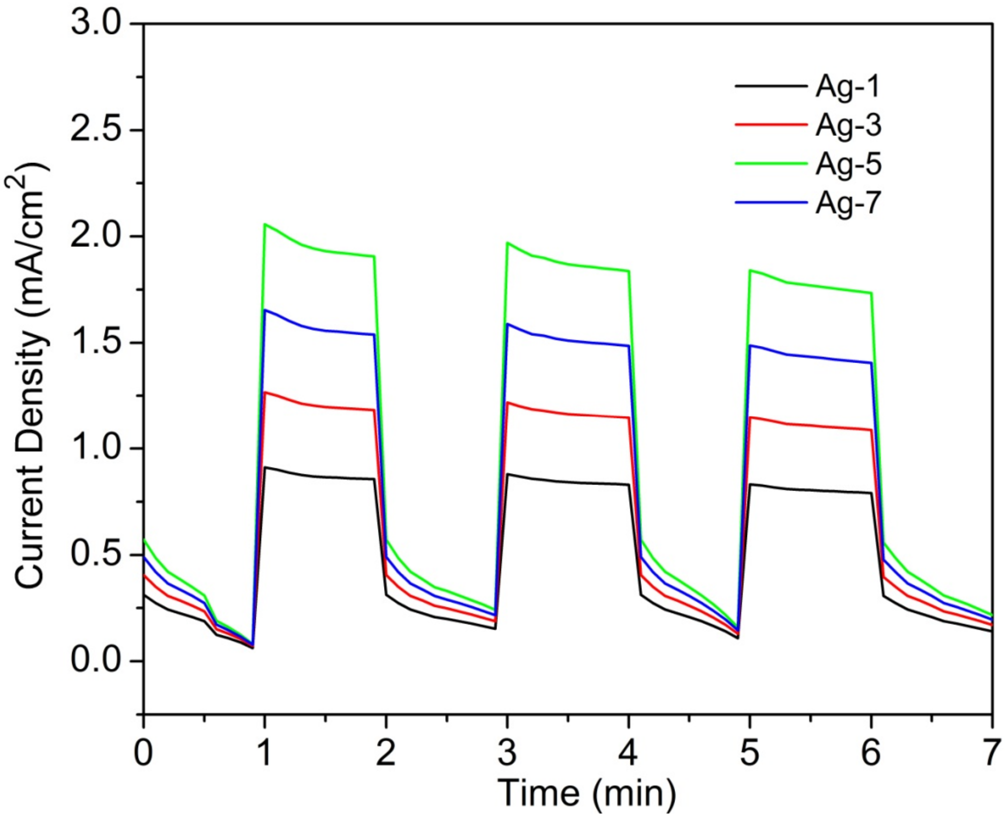


Fig. S5: Transient photocurrent response with 1 min interval of visible light exposure

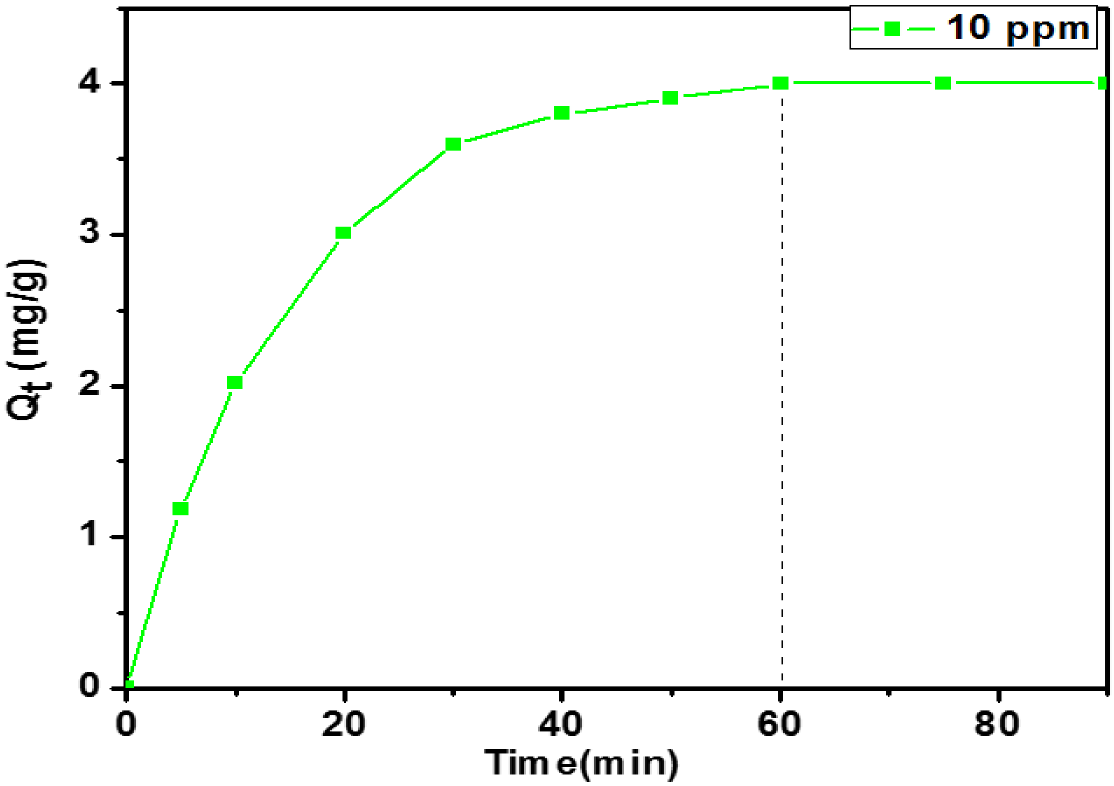


Fig. S6: Adsorption isotherm under dark

The adsorption kinetics data was plotted against the function of the time for initial CLQ concentration of 10 mg/L. Catalyst-CLQ mixture solution was prepared by adding 50 mg of catalyst was thoroughly mixed with 200 mL CLQ degradation (10 ppm, pH 7) solution. Then mixture was added inside the annular space of the reactor. The reaction was performed under dark condition for 60 min to reach adsorption equilibrium (Figure 20). During the reaction we maintain uniform mixing and constant dissolved oxygen by bubbling air from the bottom of the reactor at a flow rate of 1 LPM.

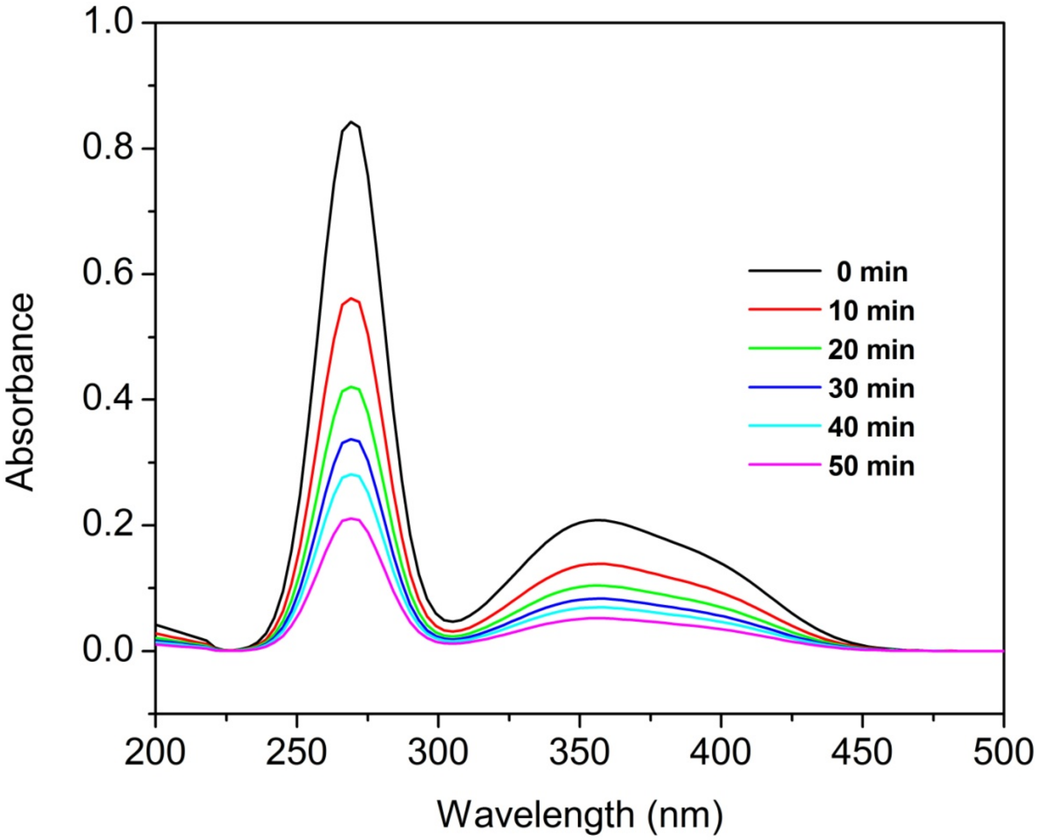


Fig. S7: Degradation of clioquinol with time

Experimental setup:

The photocatalytic degradation of CLQ was studied in a 500 mL cylindrical glass reactor. A CFL lamp (λ > 400 nm, Philips, India) with a cutoff filter was planted inside a quartz tube mounted centrally on the pivot of the reactor. All photodegradation experiments were carried out inside the annular space and the reaction blend was fomented by moderate air of 0.5 LPM at the base of the reactor by a peristaltic pump. First, CLQ was dissolved in 200 mL water, in which 0.05 g of SINP was dispersed by sonication. The initial concentration of CLQ was kept at around 20 ppm for all experimental studies. The suspension was then mixed vigorously in the absence of light for 2 h to achieve adsorption–desorption equilibrium. After irradiation, 3 mL of sample was collected every 15 min and centrifuged at 10, 000 rpm for 10 min. The supernatant was transferred to a quartz cuvette and analyzed by a UV–vis spectrophotometer.

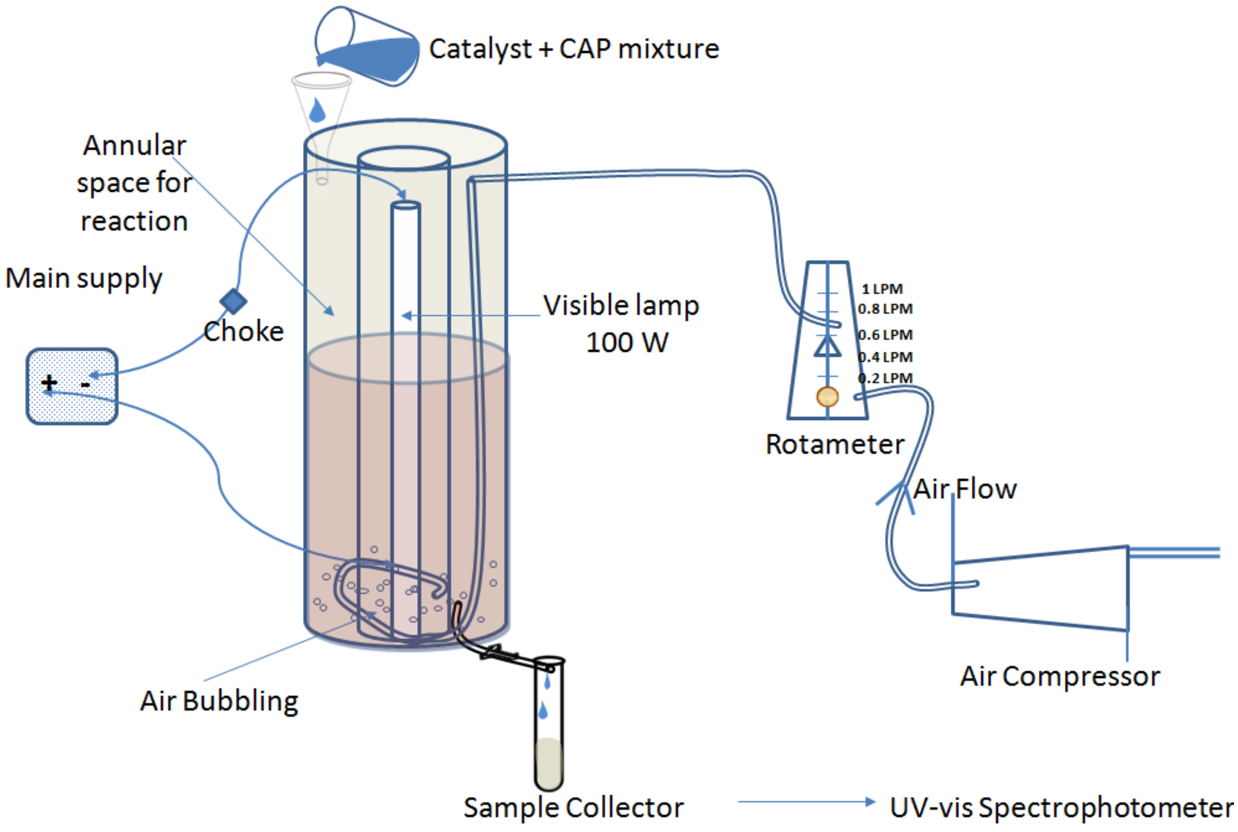


Fig. S8: Photocatalytic Experimental Set up

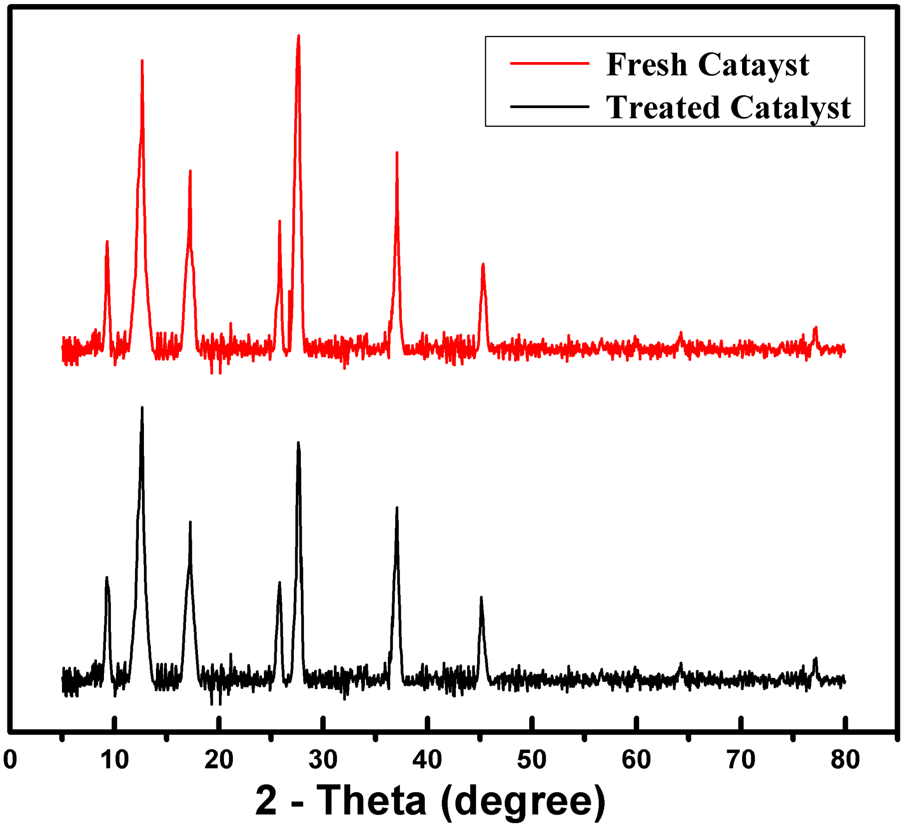
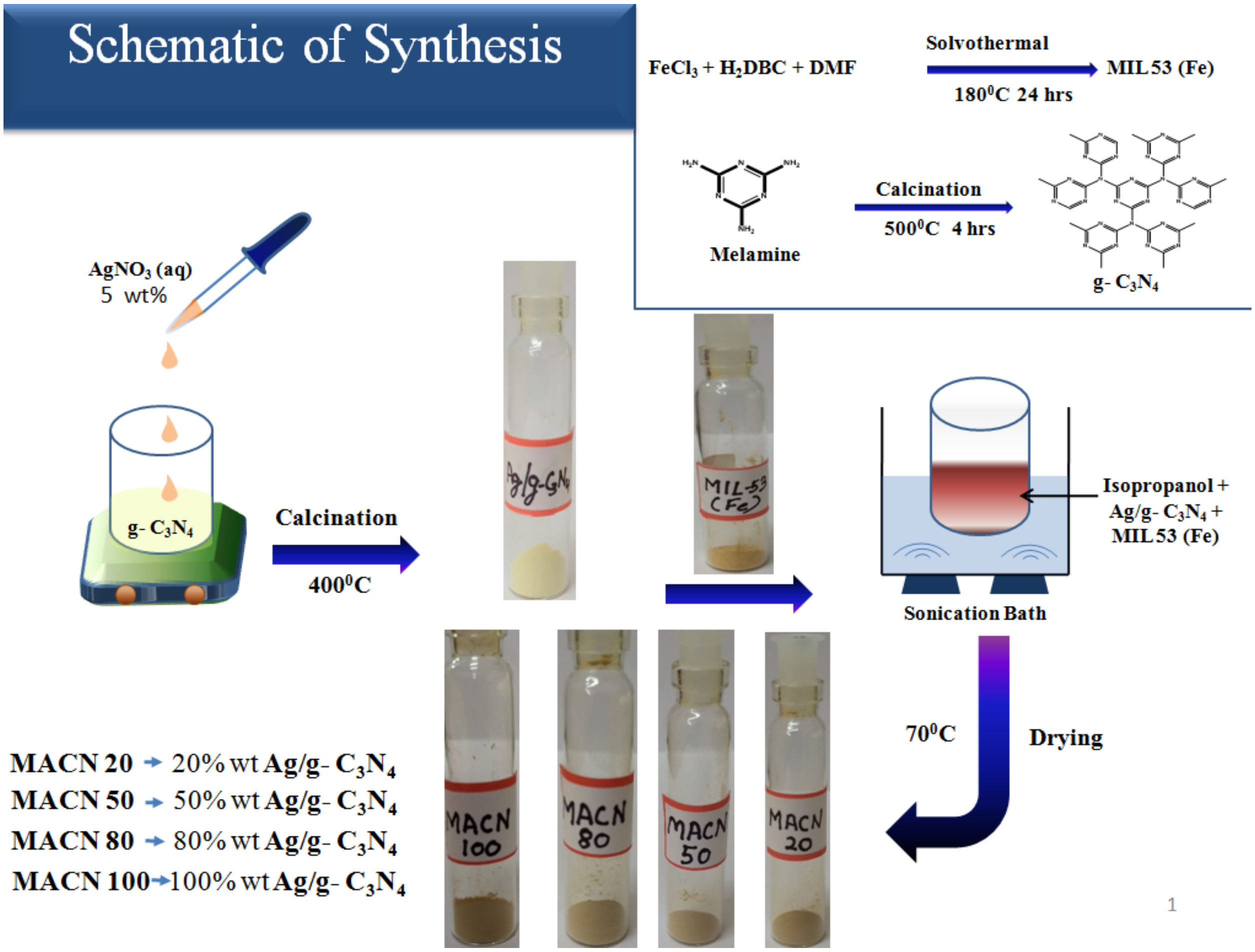


Fig. S9: Photocatalyst stability and Reusability



References

1. B. Tejerina, UV/Vis Spectra simulator, 2014, https://nanohub.org/resources/uvspec.
2. ALOthman, Z.A., A Review: Fundamental Aspects of Silicate Mesoporous Materials, Materials 2012, 5, 2874-2902.