Supplementary Information

Fabrication of different morphologies of ZnO superstructures in presence of synthesized ethylammonium nitrate (EAN) ionic liquid: Synthesis, characterization and analysis

Somnath Das and Sumit Ghosh*

Unilever R&D, Bangalore, 64, Main Road, Whitefield, Bangalore-560066

Corresponding Author: +91 80 398 31283, Fax: +91 80 2845 3086
E-mail: sumit07ghosh@hotmail.com

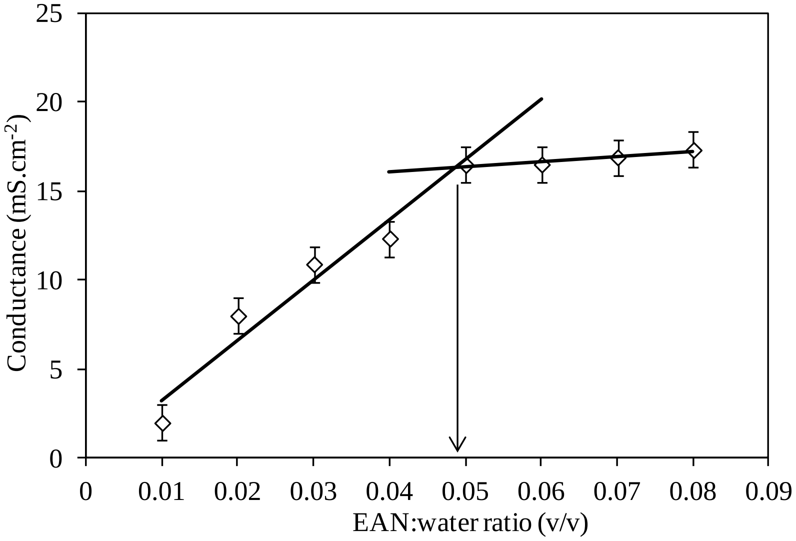


Figure S1. Profile of specific conductivity (mS.Cm^{-2}) with respect to different EAN: water (v/v) ratio ranging from 0 to 0.09 to find the CAC of EAN in water at 25°±0.5°C.

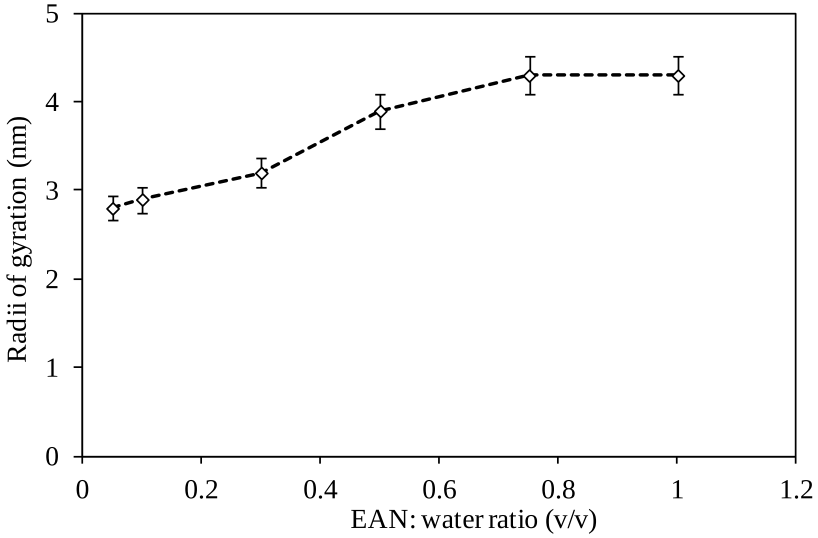


Figure S2. Radii of gyration (nm) with respect to EAN: water (v/v) ratio ranging from 0.05 to 1.0 at 25°±0.5°C.

Calculation details for the scattering experiment:

The data was fitted using Guinier plot with quadratic fit.[31] Radius of gyration (R_g) was calculated from elastic part I(q) of scattered intensity using following equation:

$$\ln I = \ln I_0 - \frac{1}{3} q^2 R_g^2 \qquad (1)$$

Where, I is the scattering intensity and I_0 is the scattering intensity at q=0.
Here, q is the wave vector, defined in following equation:

$$q = \frac{4\pi n}{\lambda} \sin\left(\frac{\theta}{2}\right) \qquad (2)$$

Where, λ is the wavelength of incident beam (488 nm), θ is scattering angle, and n is refractive index of media. Statistical average was done for each measurement while fitting data.

1 I. Otsuka, K. Fuchise, S. Halila, S. Fort, K. Aissou, I. Pignot- Paintrand, Y. Chen, A. Narumi, T. Kakuchi and R. Borsali, *Langmuir*, 2009, **26**, 2325-2332.

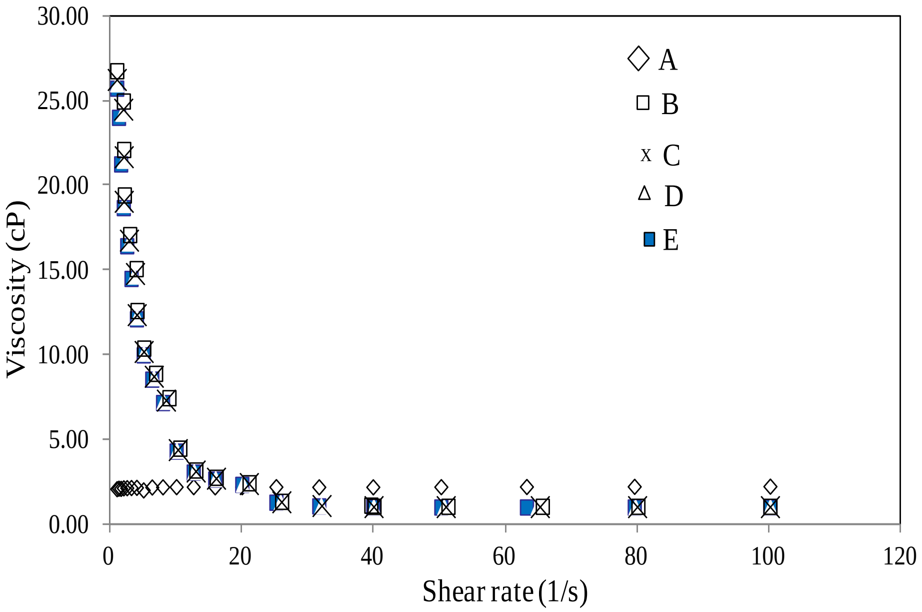


Figure S3. Variation of steady state viscosity with respect to shear rate (1/s) for EAN: water samples [A] 0.01, [B] 0.05, [C] 0.11, [D] 0.33, [E] 1 at 25°C.

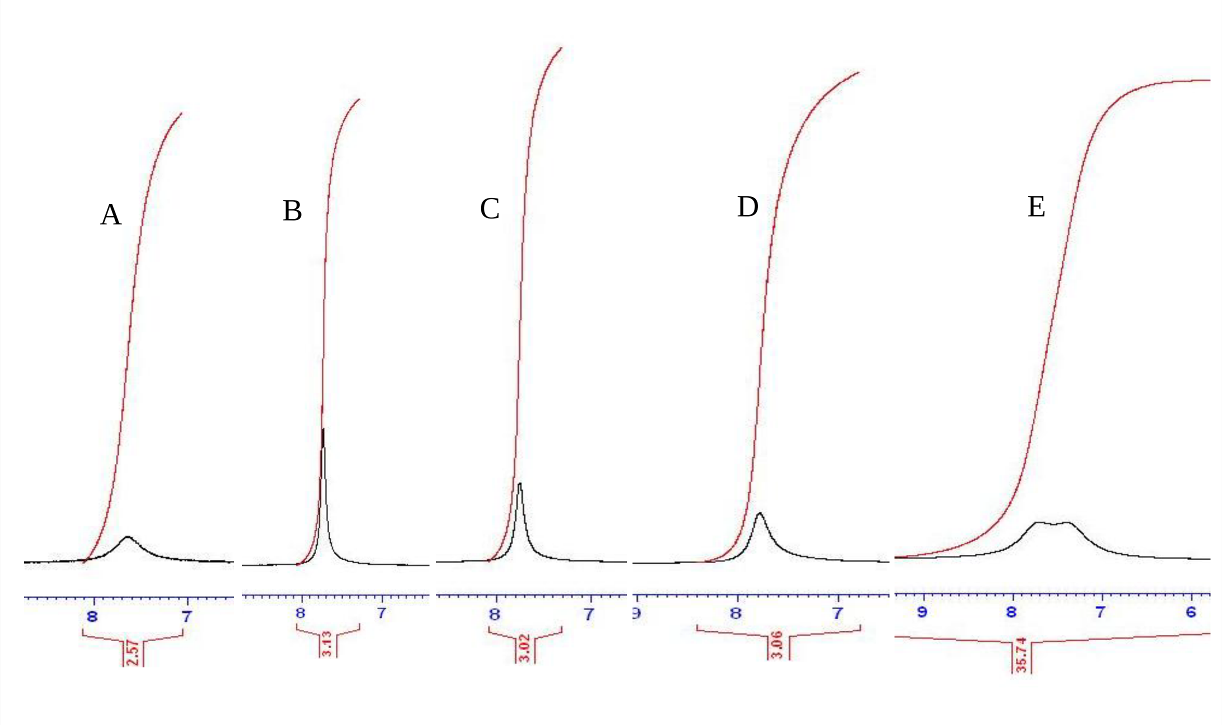
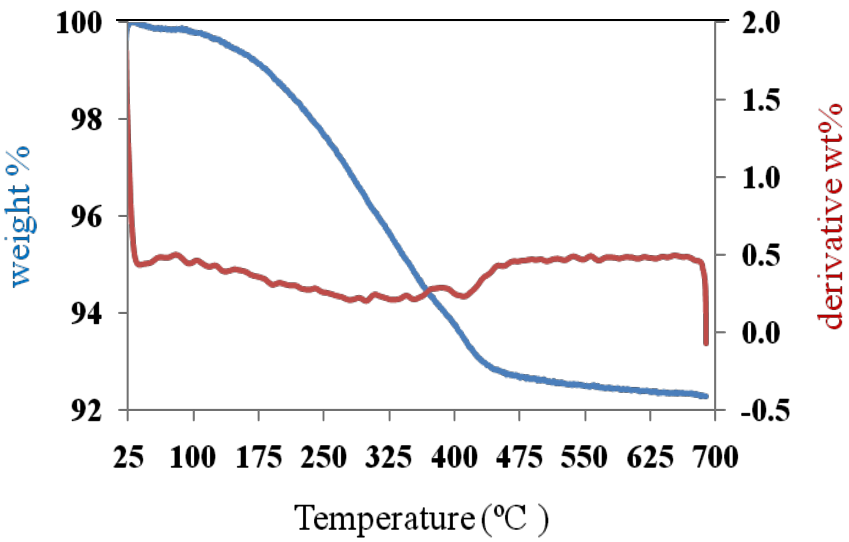


Figure S4. ^{1}H NMR spectra of the amine hydrogens of different EAN: DMSO-d_6 ratios at room temperature [A] 0.01, [B] 0.05, [C] 0.11, [D] 0.33, and [E] 1.0 whereas DMSO-d_6 was used as external lock and referenced to TMS.



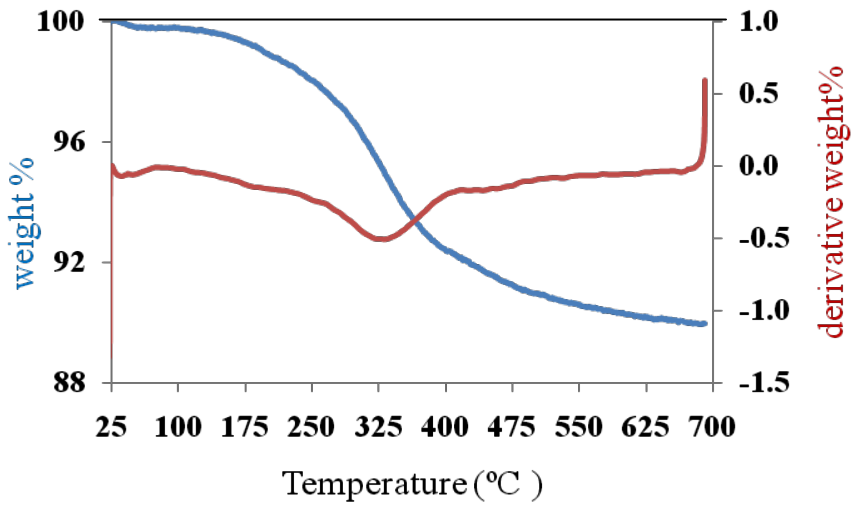


Figure S5(a): TGA profile of the ZnO sample (amorphous sample) prepared in EAN: water (v/v) ratio 1.0 at 95°C for 24 hours.

S5(b): TGA profile of the ZnO sample prepared in EAN: water (v/v) ratio 0.11 at room temperature (25°C) for 24 hours.

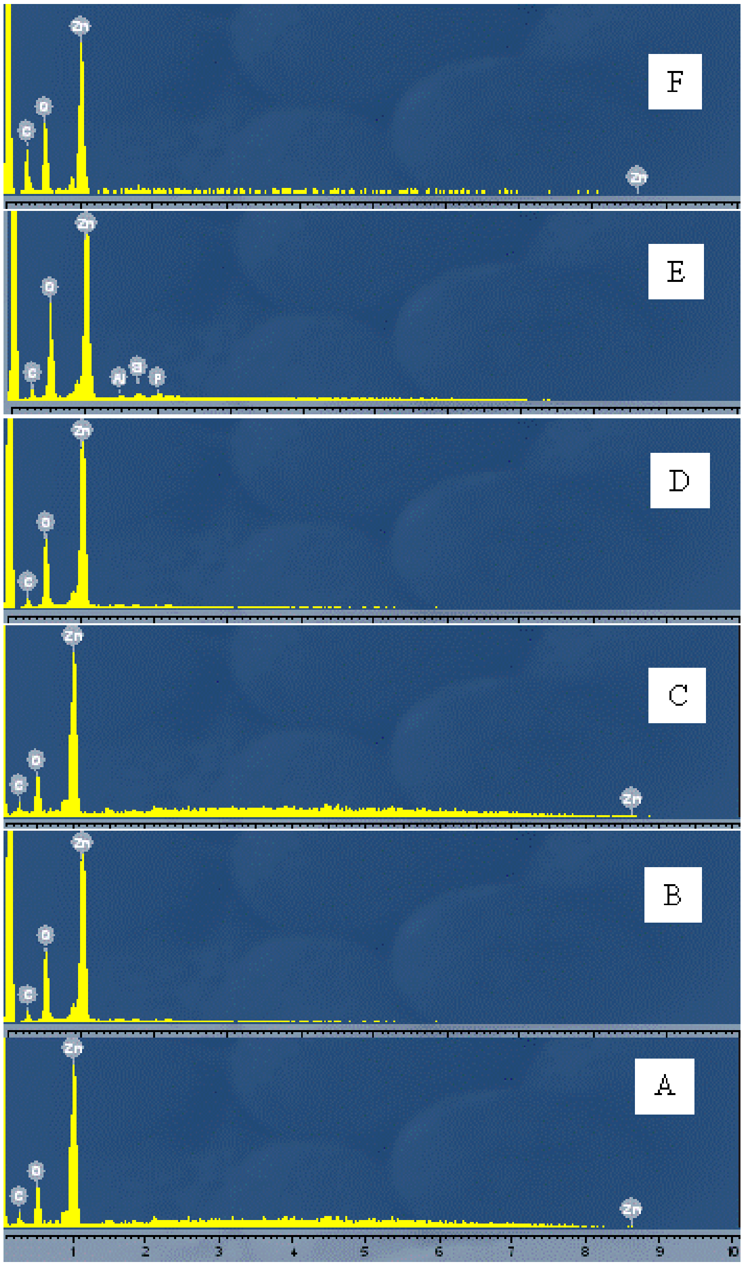


Figure S6: EDXA profiles of the ZnO samples corresponding to EAN: water (v/v) ratio where, [A] 0, [B] 0.01, [C] 0.05, [D] 0.11, [E] 0.33, and [F] 1.0 synthesized at 95°C for 24 hours.

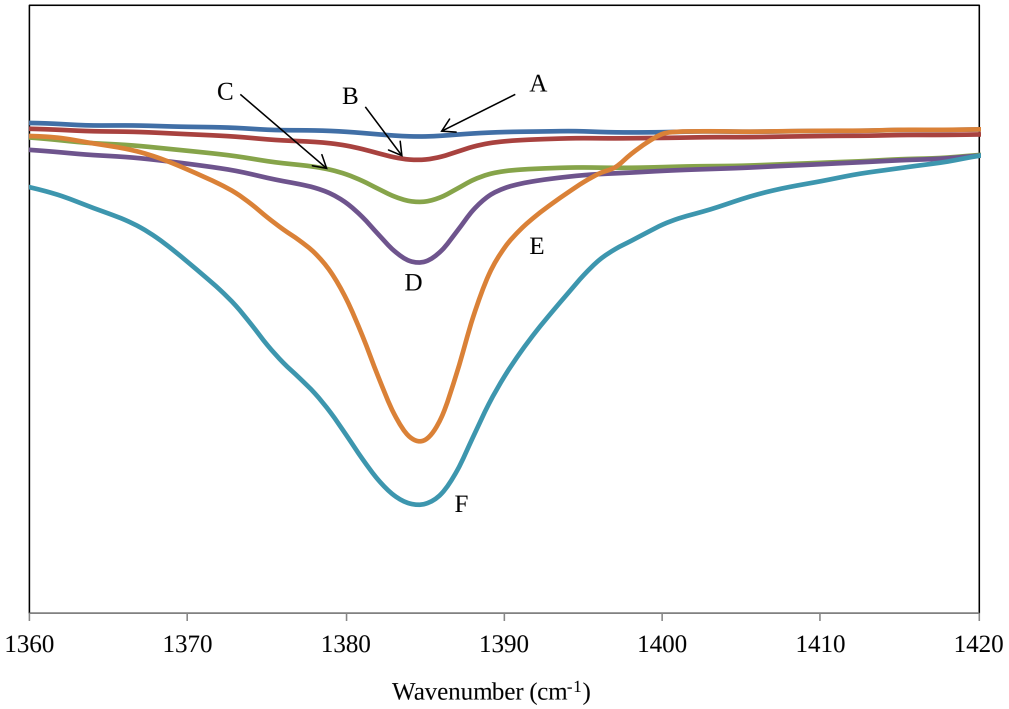


Figure S7: FTIR spectra of the ZnO samples synthesized at 95°C for 24 hours where EAN: water (v/v) ratio was varied as [A] 0, [B] 0.01, [C] 0.05, [D] 0.11, [E] 0.33 and [F] 1.0 (amorphous sample).

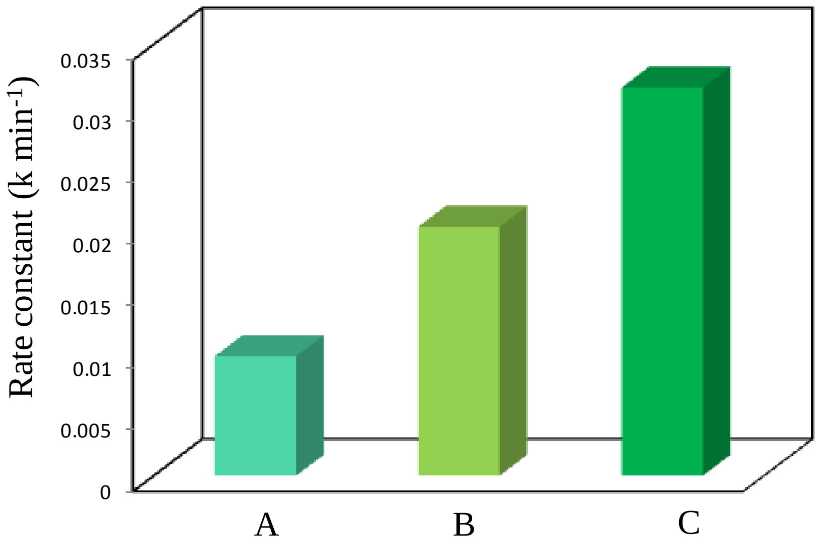


Figure S8. Rate constants for the photodegradation process of methylene blue in water (A) without any catalyst, (B) in presence of commercially available ZnO, (C) in presence of synthesized spherical ZnO (sample D).

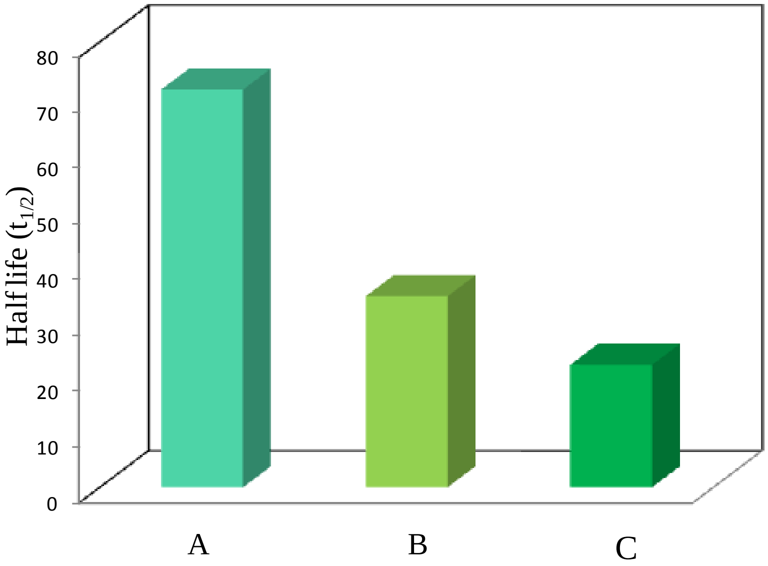


Figure S9. Half-lives ($t_{1/2}$) for the photodegradation process of methylene blue in water (A) without any catalyst, (B) in presence of commercially available ZnO, (C) in presence of synthesized spherical ZnO (sample D).

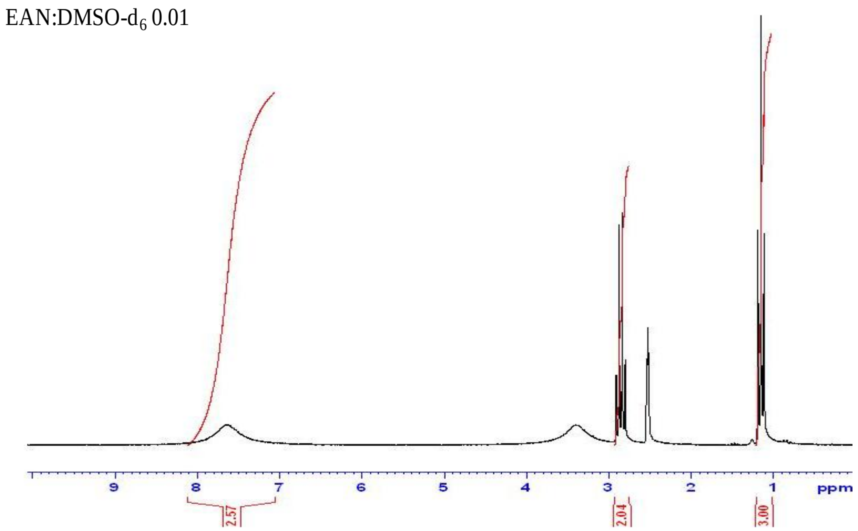


Figure S10a: ^{1}H NMR spectrum of EAN: DMSO-d_6 0.01 referenced to TMS. (^{1}H NMR, 200 MHz, DMSO-d_6, δ): 7.651 ppm (s, $-NH_3$, 3H), 2.856 ppm (m, CH_3CH_2-, -2H), 1.159 (t, CH_3CH_2-, -3H)

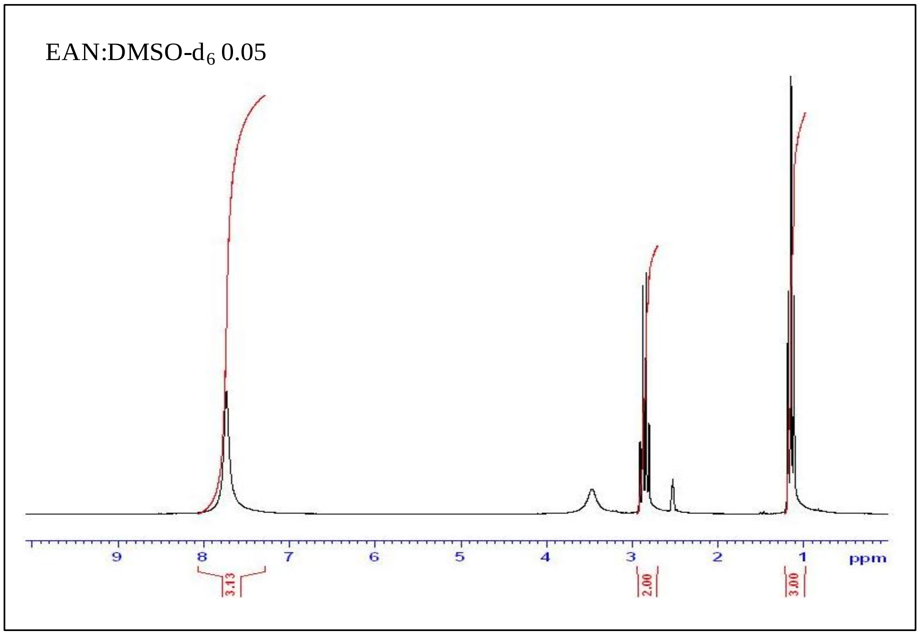


Figure S10b: ^{1}H NMR spectrum of EAN: DMSO-d_6 0.05 referenced to TMS. (^{1}H NMR, 200 MHz, DMSO-d_6, δ): 7.732 ppm (s, $-NH_3$, 3H), 2.871 ppm (m, CH_3CH_2-, -2H), 1.162 (t, CH_3CH_2-, -3H).

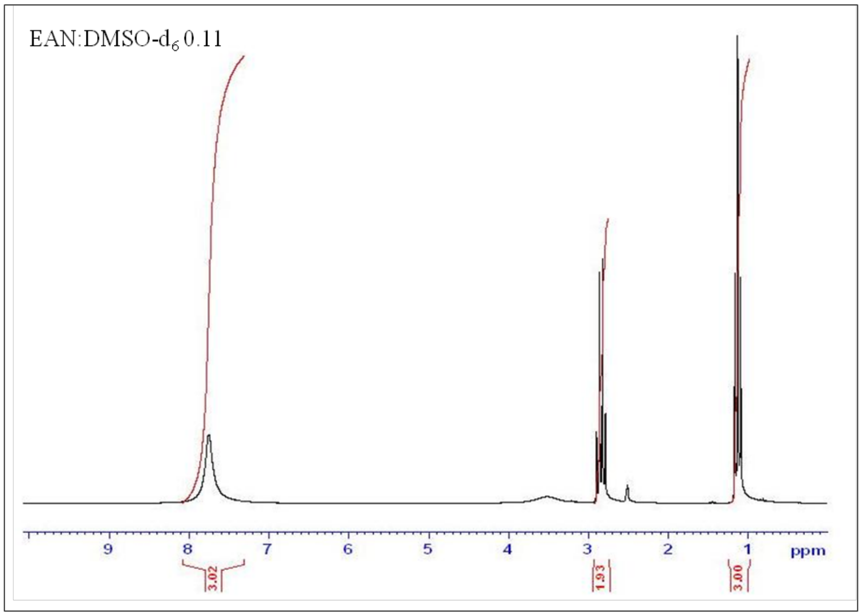


Figure S10c: ^{1}H NMR spectrum of EAN: DMSO-d_6 0.11 referenced to TMS. (^{1}H NMR, 200 MHz, DMSO-d_6, δ): 7.756 ppm (s, -NH_3, 3H), 2.887 ppm (m, CH_3CH_2-, -2H), 1.182 (t, CH_3CH_2-, -3H).

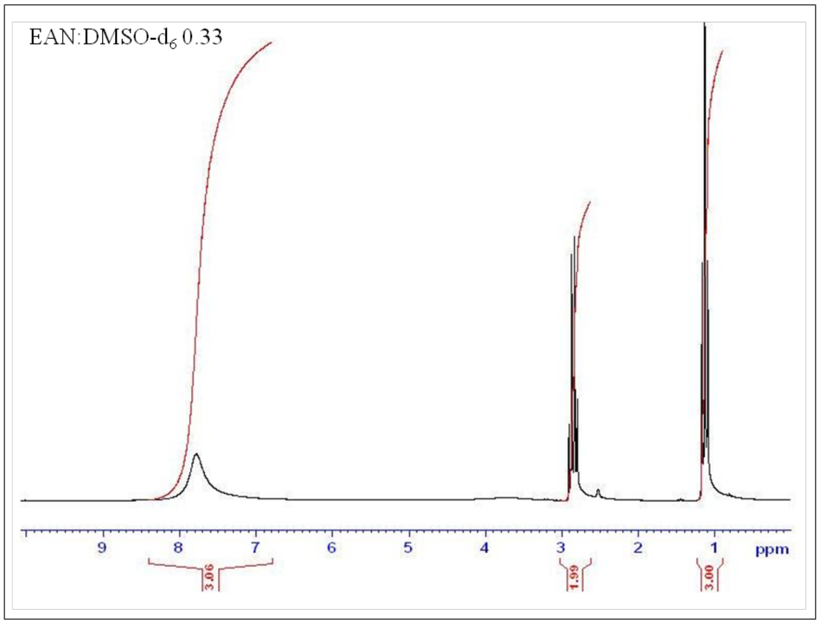


Figure S10d: ^{1}H NMR spectrum of EAN: DMSO-d_6 0.33 referenced to TMS. (^{1}H NMR, 200 MHz, DMSO-d_6, δ): 7.792 ppm (s, -NH_3, 3H), 2.895 ppm (m, CH_3CH_2-, -2H), 1.187 (t, CH_3CH_2-, -3H).

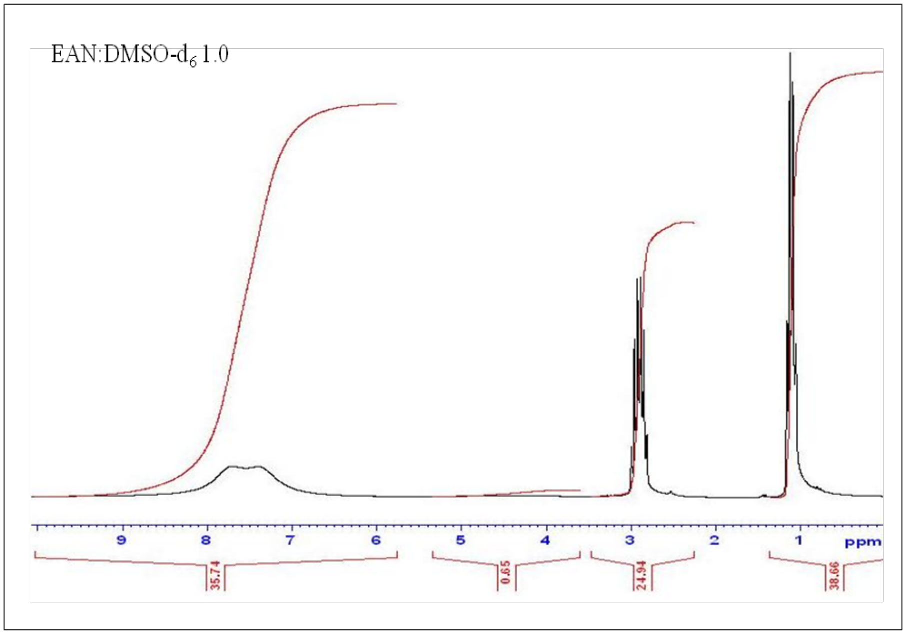


Figure S10e: ^{1}H NMR spectrum of EAN: DMSO-d$_6$ 1 referenced to TMS. (^{1}H NMR, 200 MHz, DMSO-d$_6$, δ): 7.801 ppm, 7.345 ppm (d, -NH$_3$), 2.895 ppm (m, CH$_3$CH$_2$-, -2H), 1.187 (t, CH$_3$CH$_2$-, -3H).

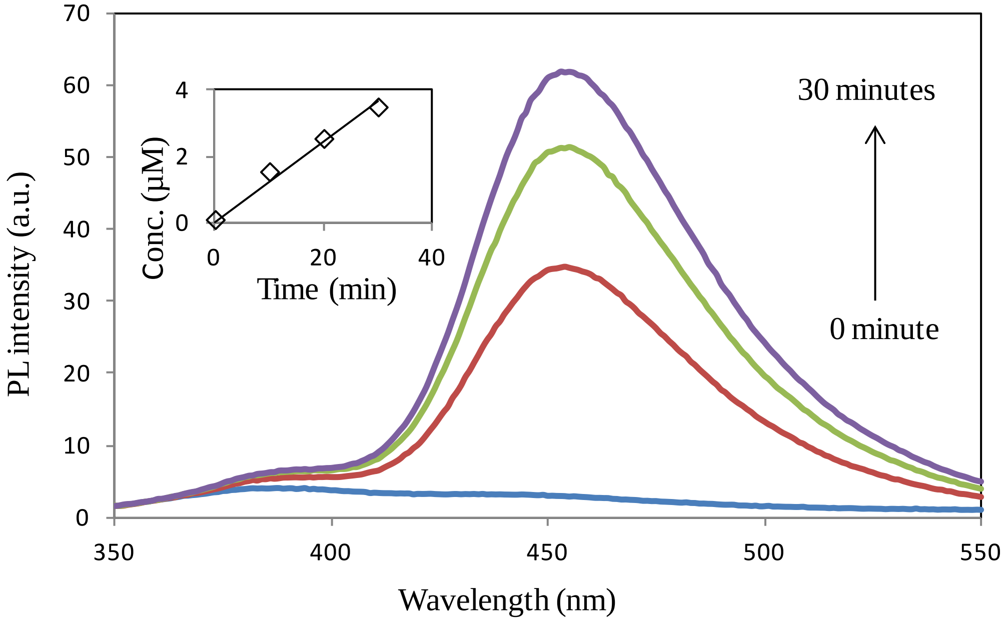


Figure S11: PL spectral change observed during the illumination of TiO$_2$ dispersed in 1mM Coumarin aqueous solution. Each fluorescence spectrum was recorded every 10 minutes of Xenon lamp illumination. Inset shows the plots of concentration of hydroxyl radical produced on the irradiated TiO$_2$ against irradiation time.

Experimental details for measuring the photocatalytic efficiency of the synthesized ZnO (sample [D], Table 1):

Hydroxyl radicals are responsible for the photocatalytic activities. Q. Xian and co-workers developed a method by which the photocatalytic activities of different samples can be measured using photoluminescence technique based on the formation of fluorescence active 7-hydroxy coumarin from fluorescence inactive coumarin upon irradiation and in presence of catalyst. The principle, calculation method and equations, as well as the details of background theory can be found in the report of Q. Xian and co-workers.[2] The photoluminescence spectra were recorded in the S-5700 spectrofluoremeter, fixing the emission and excitation slit-widths at 5 nm. The excitation wavelength was kept fixed at 332 nm and the samples were scanned from 350 nm to 550 nm. The working equation for calculating the OH-index is as follows:

OH-index = $(r/r_0)\times 100$,

Where ‘r’ is the rate of formation of hydroxyl radical with the experimental sample after irradiation in presence of coumarin solution, ‘r_0’ is the rate of formation of hydroxyl radical with TiO_2 (Degussa, P25) after irradiation in presence of coumarin solution.

2 Q. Xiang, J. Yu and P. K. Wong, *J. Colloid Interf. Sci.*, 2011, **357**, 163-167.