

## ***One-pot sustainable preparation of sunlight active ZnS@Graphene nano-composite using Zn containing surface active ionic liquid***

Komal Arora,<sup>a</sup> Gurbir Singh,<sup>b</sup> Sekar Karthikeyan,<sup>c</sup> Tejwant Singh Kang,<sup>\*, a</sup>

<sup>a</sup> *Department of Chemistry, UGC-centre for Advance Studies – II, Guru Nanak Dev University, Amritsar, 143005, India.*

<sup>b</sup> *Department of Earth Resources Engineering, Faculty of Engineering, Kyushu University, 744 Motoooka, Nishiku, Fukuoka 819-0395, Japan.*

<sup>c</sup> *Department of Chemistry and Biochemistry, Graduate School of Engineering, Kyushu University, 744 Motoooka, Nishi-ku, Fukuoka 819-0395, Japan.*

### Supporting Information

*\*To whom correspondence should be addressed: E-mail: [tejwantsinghkang@gmail.com](mailto:tejwantsinghkang@gmail.com); [tejwant.chem@gndu.ac.in](mailto:tejwant.chem@gndu.ac.in) Tel: +91-183-2258802-Ext-3192*

## Annexure S1

### HPLC calibration

CIP was analysed using a high performance liquid chromatography (HPLC) system (JASCO UV plus 2075, Japan) coupled with UV/Vis detector selected at  $\lambda=254$  nm and a Shodex C18M 4E analytical column (4.6 I.D  $\times$  250 mm), separation factor ( $\alpha_1=2.42$  and  $\alpha_2=1.47$ ) with a constant temperature of 25°C and pressure maximum 20 MPa and minimum 0.2 MPa. The eluent consists of 60:10:30 (v/v) acetonitrile: water: formic acid (25mM) (TCI, Japan) with a flow rate of 0.6mL/min. The formulas used to determine apparent quantum efficiency are provided in Annexure S1, Electronic Supporting Information, ESI.

### Apparent quantum efficiency (AQE) determination

$$\text{Apparent quantum efficiency (\%)} = \frac{\text{Mols of reacted electrons per unit time}}{\text{Mols of incident photons per unit time}} \times 100 \quad (\text{S1})$$

$$\text{Mols incident photons per unit time (N}_{\text{Einstein}}) = \frac{\text{Number incident photons per unit time}}{N_A}$$

Number of incident photons  $N_p$  per unit time can be calculated by:

$$N_p = \frac{\text{Intensity (E)}}{\text{Photon energy (E}_p)} \quad \text{and} \quad \text{photon energy (E}_p) = \frac{hc}{\lambda} \quad (\text{S2})$$

E = Irradiance  $\times$  reactor area illuminated

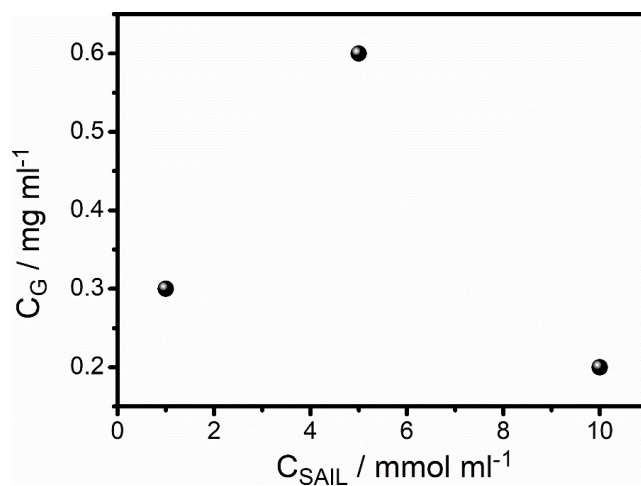
$$E_p = \frac{(6.625 \times 10^{-34} \text{ J.s})(3 \times 10^{17} \text{ nm.s}^{-1})}{\lambda(\text{nm})} = \frac{19.88 \times 10^{-17}}{\lambda(\text{nm})} = 4.73 \times 10^{-19} \text{ J} \quad (\text{S3})$$

$$N_p = \frac{E}{E_p} = \frac{0.00189}{4.73 \times 10^{-19}} = 1.73 \times 10^{16} \quad \text{J}$$

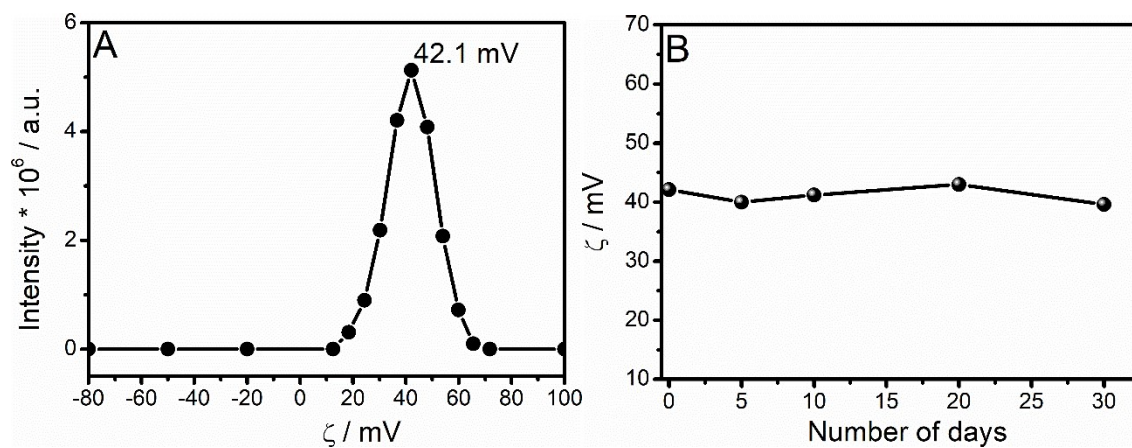
(S4)

$$N_{\text{Einstein}} = \frac{N_p}{N_A} = 2.87 \times 10^{-6} \quad \text{mols.s}^{-1}$$

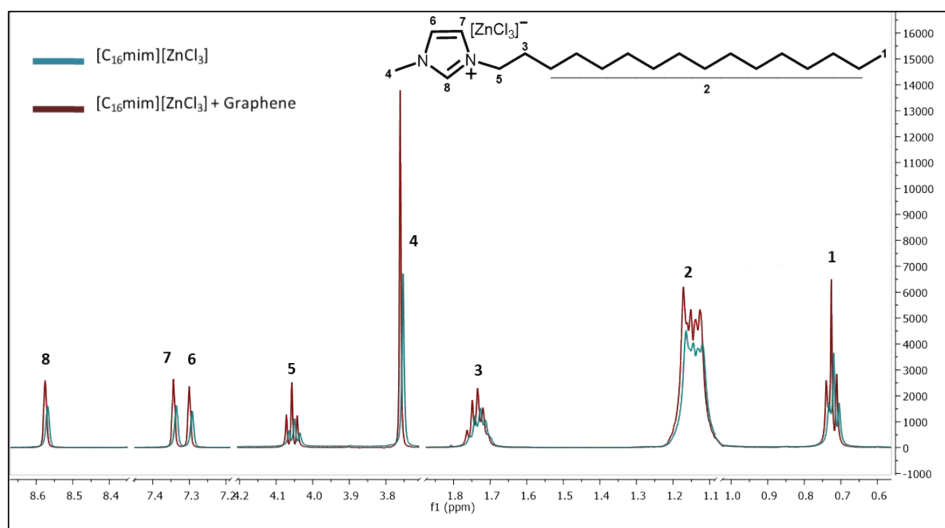
(S5)



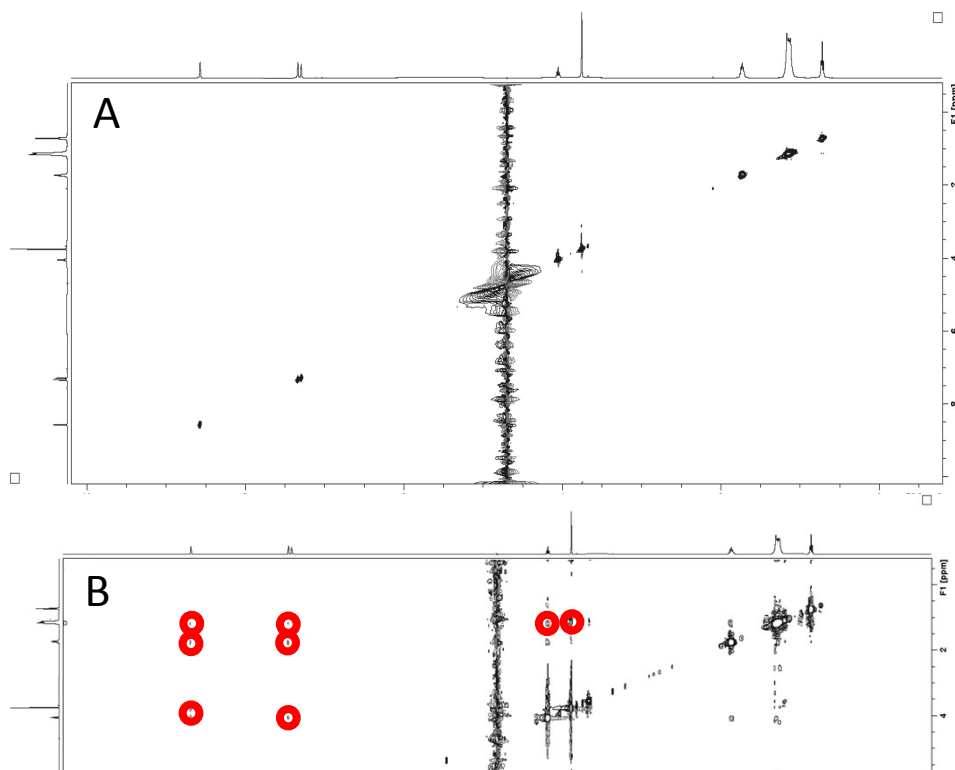
**Figure S1:** Concentration of exfoliated graphene ( $C_G$ ) as a function of concentration of  $[\text{C}_{16}\text{mim}][\text{ZnCl}_3]$ .



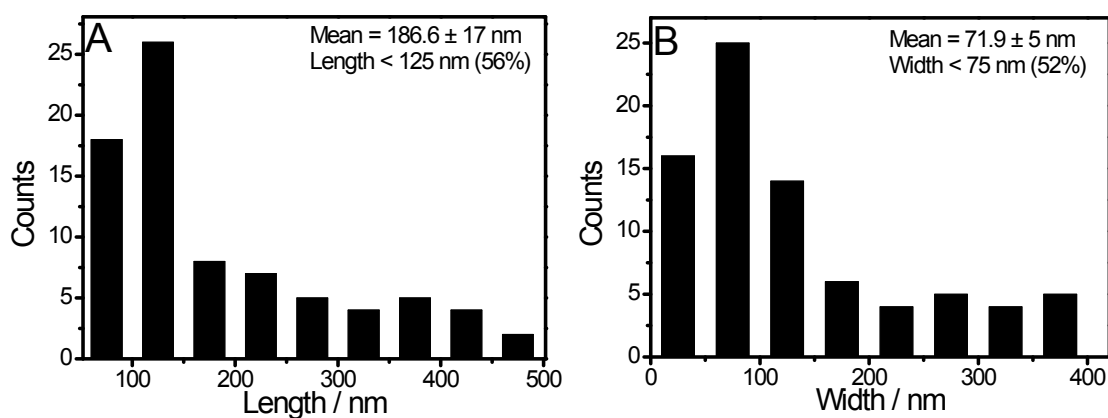
**Figure S2:** (A) Zeta ( $\zeta$ ) potential value of graphene dispersion in aqueous solution of SAIL at concentration of 5 mmol L<sup>-1</sup>; (B) Variation of  $\zeta$ -potential of graphene dispersion in aqueous solution of 5 mmol L<sup>-1</sup> concentration of SAIL as a function of days



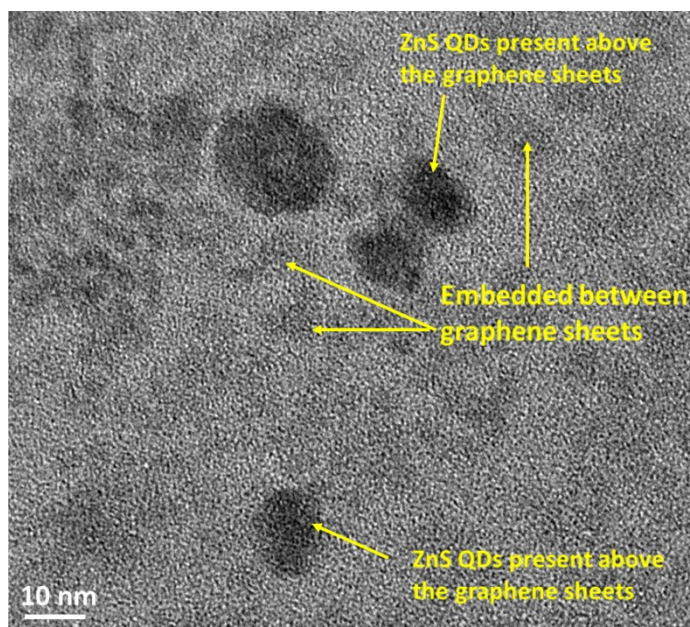
**Figure S3:** <sup>1</sup>H NMR spectra of MIL in 10% D<sub>2</sub>O with and without graphene.



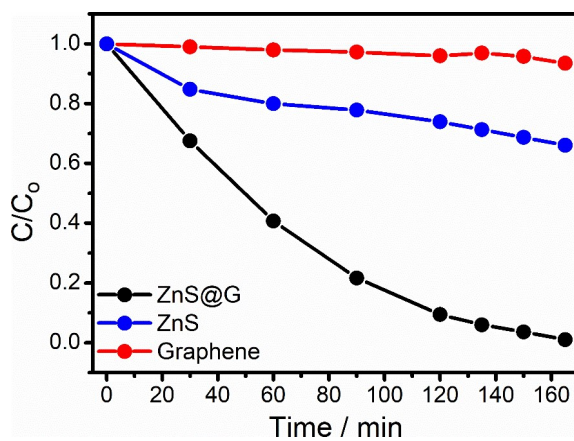
**Figure S4:** (A) 2D  $^1\text{H}$ - $^1\text{H}$  NOESY spectra of aqueous solution of  $[\text{C}_{16}\text{mim}][\text{ZnCl}_3]$  in absence of graphene; (B) 2D  $^1\text{H}$ - $^1\text{H}$  NOESY spectra of aqueous solution of  $[\text{C}_{16}\text{mim}][\text{ZnCl}_3]$  in the presence of graphene. Red circles in B shows the presence of correlation peaks between the alkyl chain of  $[\text{C}_{16}\text{mim}][\text{ZnCl}_3]$ .



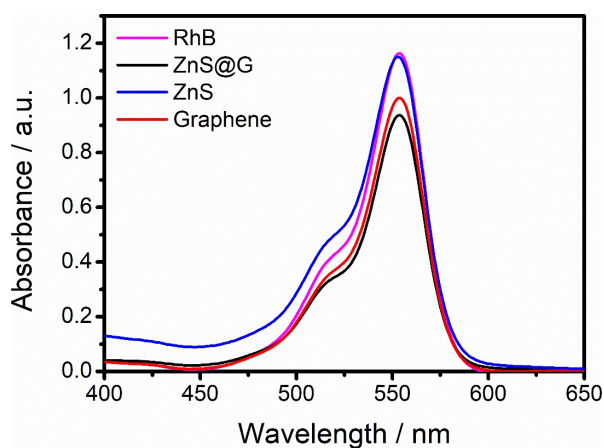
**Figure S5:** Statistical data of (A) length and; (B) width obtained from analysis of AFM images of graphene sheets.



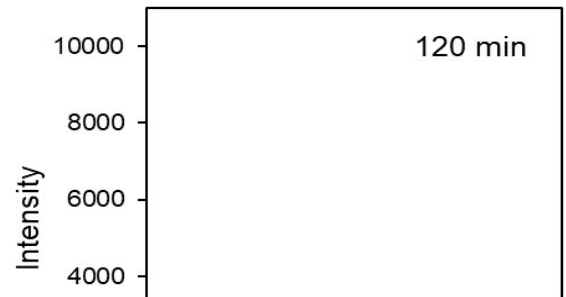
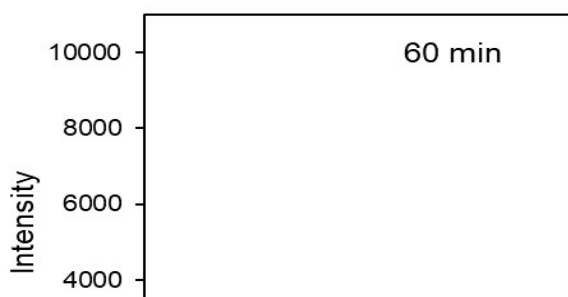
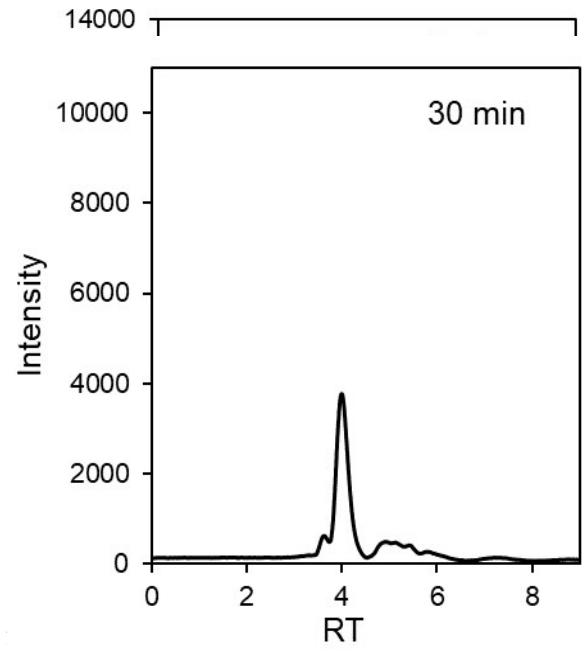
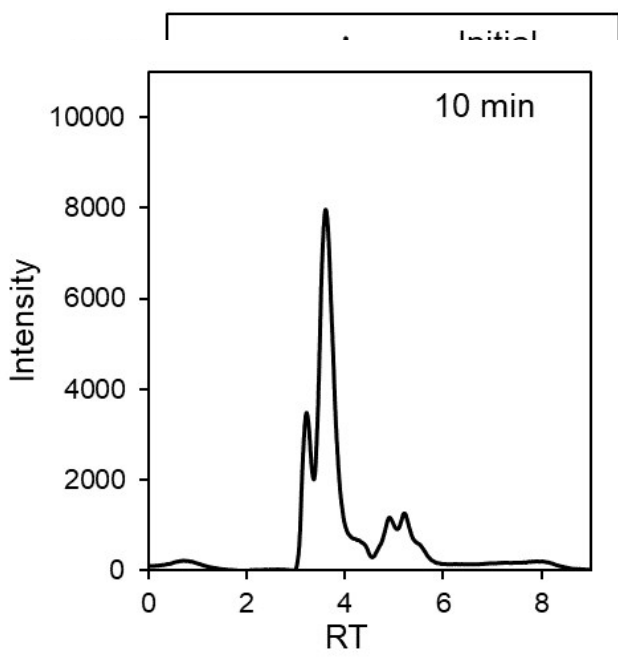
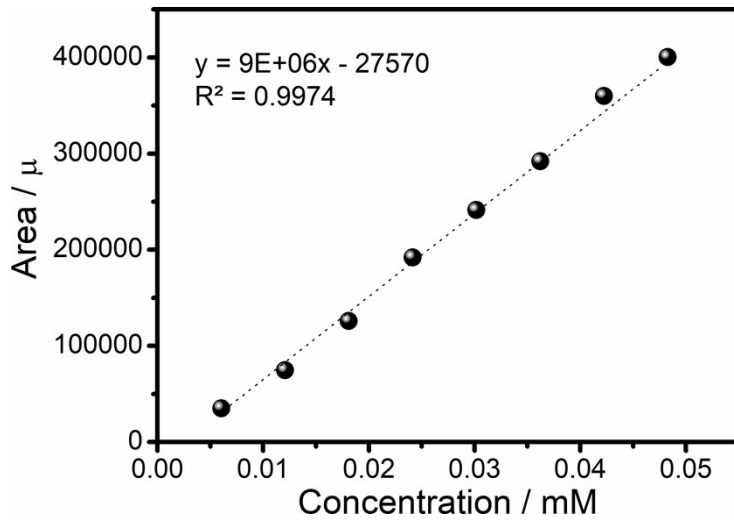
**Figure S6:** TEM image of prepared ZnS@G NCs showing ZnS QDs embedded between the graphene sheets and present above the graphene sheet.



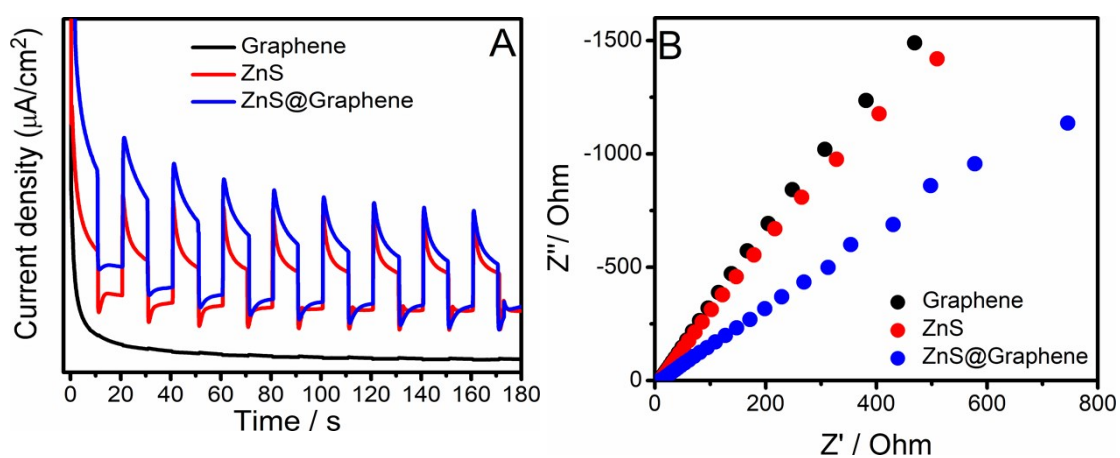
**Figure S7:** Catalytic performance of ZnS@G NCs, ZnS QDs and Graphene towards the degradation of RhB dye under sun light.



**Figure S8:** Variation in absorbance spectra of RhB dye using ZnS@G NCs and its counterparts after stirring for 30 min in dark.



**Figure S10:** HPLC spectra of CPI at different time intervals in the presence of ZnS@G NC under visible light.



**Figure S11:** (A) Transient photocurrent; (B) EIS (Nyquist) plot at 0 V vs. RHE under illumination of ZnS@Graphene, ZnS, and Graphene.